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Determination of Stable Valence States of Chromium in Aqueous and Solid Waste Matrices - Experimental Verification of Chemical Behavior

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DETERMINATION OF STABLE VALENCE STATES OF CHROMIUM IN AQUEOUS AND SOLID WASTE MATRICES - EXPERIMENTAL VERIFICATION OF CHEMICAL BEHAVIOR

by

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The objective of this research effort was to experimentally assess the chemical behavior of the stable species of chromium during the preparation, chemical manipulation, and spectrophotometric analyses of simulated and authentic environmental samples for hexavalent chromium.

The diphenylcarbazide colorimetric method was found to be specific and sensitive for Cr(VI), as either dichromate or chromate, in simulated aqueous solutions containing up to 1000-fold ratios of Cr(III). Problems of reduction were encountered with the method for analyses of simulated samples containing excesses of both Cr(III) and sulfide. Studies of selected digestion methods for the analyses of insoluble chromates revealed that the alkaline digestion generally provided satisfactory recoveries of Cr(VI) however, the nitric acid digestion was inadequate for the conditions studied. Although Cr(VI) spikes were stable in alkaline digests of most of the environmental samples studies, Cr(III) spikes were found to be partially oxidized in the alkaline digests, resulting in positive errors by as much as 100% in Cr(VI) measurements.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, Ohio conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report presents the results of the evaluation of U.S. EPA Method 3060, "Alkaline Digestion for Hexavalent Chromium" and Method 7196, "Spectrophotometric Method for Hexavalent Chromium".

Robert L. Booth, Director
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ABSTRACT

The objective of this research effort was to experimentally assess the chemical behavior of the stable species of chromium during the preparation, chemical manipulation, and spectrophotometric analyses of simulated and authentic environmental samples for hexavalent chromium. The effort for this research was divided into four experimental phases, addressing specific objectives: (1) characterization and ruggedness evaluation of the diphenylcarbazide (DPC) spectrophotometric method for hexavalent chromium, (2) evaluation of the stability and reactivity of hexavalent chromium under simulated, but controlled aqueous matrix conditions, (3) evaluation of alkaline and acidic digestions for the analysis of insoluble chromate standards and trivalent chromium, and (4) evaluation of alkaline and acidic digestions for chromium analyses of environment samples.

The diphenylcarbazide colorimetric method was found to be specific and sensitive for Cr(VI), as either dichromate or chromate, in simulated aqueous solutions containing up to 1000-fold ratios of Cr(III). Problems of reduction were encountered with the method for analyses of simulated samples containing excesses of both Cr(III) and sulfide. Studies of selected digestion methods for the analyses of insoluble chromates revealed that the alkaline digestion generally provided satisfactory recoveries of Cr(VI) however, the nitric acid digestion was inadequate for the conditions studied. Although Cr(VI) spikes were stable in alkaline digests of most of the environmental samples studies, Cr(III) spikes were found to be partially oxidized in the alkaline digests, resulting in positive errors by as much as 100% in Cr(VI) measurements.

Many of the environmental samples became turbid or colored during the alkaline digestion which affected the DPC colorimetric measurement of Cr(VI). To overcome this problem additional filtration and dilution was required. Such manipulations required measurements to be performed in a lower absorbance region, resulting in increased imprecision.

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SECTION 1
INTRODUCTION

The analyses of solid waste materials for hexavalent chromium represent formidable challenges to the analytical scientist. A metal speciation scheme to differentiate between trivalent and hexavalent chromium species, Cr(III) and Cr(VI), must address: (1) solubilization of chromium species from solid matrices, while (2) maintaining the integrity of the individual chromium species during all sample manipulation phases of the analytical method. Whereas much research has focused on the separation and detection of dissolved chromium species in synthetic aqueous mixtures or relatively clean liquid environmental samples, the chemical solubilization and determination of Cr(VI) in solid waste materials have not been adequately addressed. From a recent computerized literature search conducted by Battelle, only one study[1] was identified which addressed factors relevant to extractions of Cr(VI) in the presence of large excesses of Cr(III) in solid materials.

The main research efforts of this study have been directed toward method evaluation and the study of the analytical chemistry of stable chromium species during the preparation, chemical manipulation, and instrumental analyses of simulated and selected authentic environmental samples. The present study has focused on an investigation of three selected digestion methods for the chemical solubilization of Cr(VI) in barium chromate test compounds and in real environmental samples: (1) an alkaline digestion medium, consisting of an aqueous solution of sodium carbonate and sodium hydroxide, (2) a nitric acid digestion method, and (3) a nitric acid/persulfate digestion method. The relative merits of the digestion methods have been based on the analytical results for solubilization of insoluble chromates as well as stability of Cr(III) and Cr(VI) spikes in various test solutions and authentic environmental samples. The chromium chemistry encountered during sample preparation, manipulation and analyses is briefly described below.

The two stable chromium oxidation states in natural and wastewaters are 3^+ and 6^+. Hexavalent chromium in alkaline solution exists in the form of the chromate ion, CrO_4^{2-}. At acidic pH, the dichromate ion and protonated chromate ion predominates. The equilibrium is represented in the following equations:

$$2CrO_4^{2-} + 2H^+ \longleftrightarrow Cr_2O_7^{2-} + H_2O \qquad K = 4.2 \times 10^{14}$$

$$HCrO_4^- \longleftrightarrow CrO_4^{2-} + H_2O \qquad K = 3.2 \times 10^{-7}$$

The distribution of $HCrO_4^-$ and $Cr_2O_7^{2-}$ is concentration and pH dependent according to the equilibrium:

$$2HCrO_4^- \longleftrightarrow Cr_2O_7^{2-} + H_2O \qquad K = 43$$

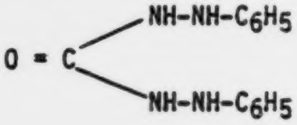
For example, at 1M total chromium concentration, the predominant species in acid solution is $Cr_2O_7^{2-}$ while CrO_4^{2-} predominates at pH higher than 7. At lower concentrations (10^{-4}M = 15 mg/L), $HCrO_4^-$ represents over 99 percent of the total chromium concentration at pH less than 4.8.[2]

Trivalent chromium existed as hexa-coordinated complexes in solution. The complex $[Cr(H_2O)6]^{3+}$ is kinetically inert due to slow ligand exchange rates. At near neutral and alkaline pH, Cr(III) ions may be precipitated as chromic hydroxide as controlled by: $Cr(OH)_{3(S)} \longleftrightarrow Cr^{3+} + 3OH^-$; $K_{sp} = 10^{-31}$. In the presence of excess base, $Cr(OH)_{3(S)}$ can be resolubilized by forming a hydroxy complex: $Cr(OH)_3 + OH^- \longleftrightarrow Cr(OH)_4^-$; $K_f = 10^{-0.4}$. With aging and heating, $Cr(OH)_3$ precipitation is promoted, presumably through polymerization.

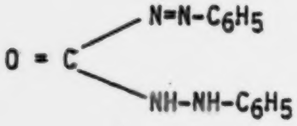
The diphenylcarbazide spectrophotometric method, as described in EPA Method 7196, was employed to measure concentration changes in hexavalent chromium for each test sample solution resulting from chromium redox phenomena occuring during the digestions. Under the present test conditions for DPC spectrophotometry, an excess molar concentration (at least 25 molar ratio excess) of diphenylcarbazide was provided for the concentration level of Cr(VI) expected in the test solutions.

In Phase I testing, the diphenylcarbazide spectrophotometric method for Cr(VI) has been evaluated under controlled environmental and analytical conditions. The diphenylcarbazide spectrophotometric method is the most established, rapid and economical of the available test methods for hexavalent chromium.[3] Diphenylcarbazide is regarded as a specific reagent for Cr(VI) in the presence of Cr(III), whereas the nonspecificity of atomic absorption spectrometry (AAS) in terms of elemental valence state requires chemical isolation of Cr(VI) prior to the quantification step. However, the diphenylcarbazide spectrophotometric method suffers from potential interferences due to matrix components such as Mo(VI), Hg(II), and V(V) species which may react to form color with the diphenylcarbazide reagent or Fe(III) which is chromophoric and forms yellow-colored solutions that absorb 540-nm radiation.

The soluble red-violet species is a chelate of Cr(III) (formed by reduction of Cr(VI) by the DPC reagent) and diphenylcarbazone (the oxidized form of DPC). The structural formulae of diphenylcarbazide and diphenylcarbazone are shown below:



sym-Diphenylcarbazide (1,5-Diphenylcarbohydrazide)



Diphenylcarbazone (Phenylazoformic acid 2-phenylhydrazide)

The chelate is of the form $[Cr^{III}(HL)_2]^+$ where H_2L is diphenylcarbazone and H_4L is diphenylcarbazide.[4-8] The reaction[2] may be written:

$$2CrO_4^{2-} + 3H_4L + 8H^+ \longrightarrow [Cr^{III}(HL)_2]^+ + Cr^{3+} + H_2L + 8H_2O$$

where H_4L is diphenylcarbazide (DPCI),
H_2L is diphenylcarbazone (DPCO), and
$[Cr^{III}(HL)_2]^+$ is the soluble, red-violet chelate of Cr(III) and DPCO formed through a redox reaction as seen in Figure 1.

Phase II and phase III of this study were designed to investigate the dynamics of the Cr(III)-Cr(VI) redox couple under various pH conditions. The electrochemical properties of aqueous chromium ions are highly pH-dependent.

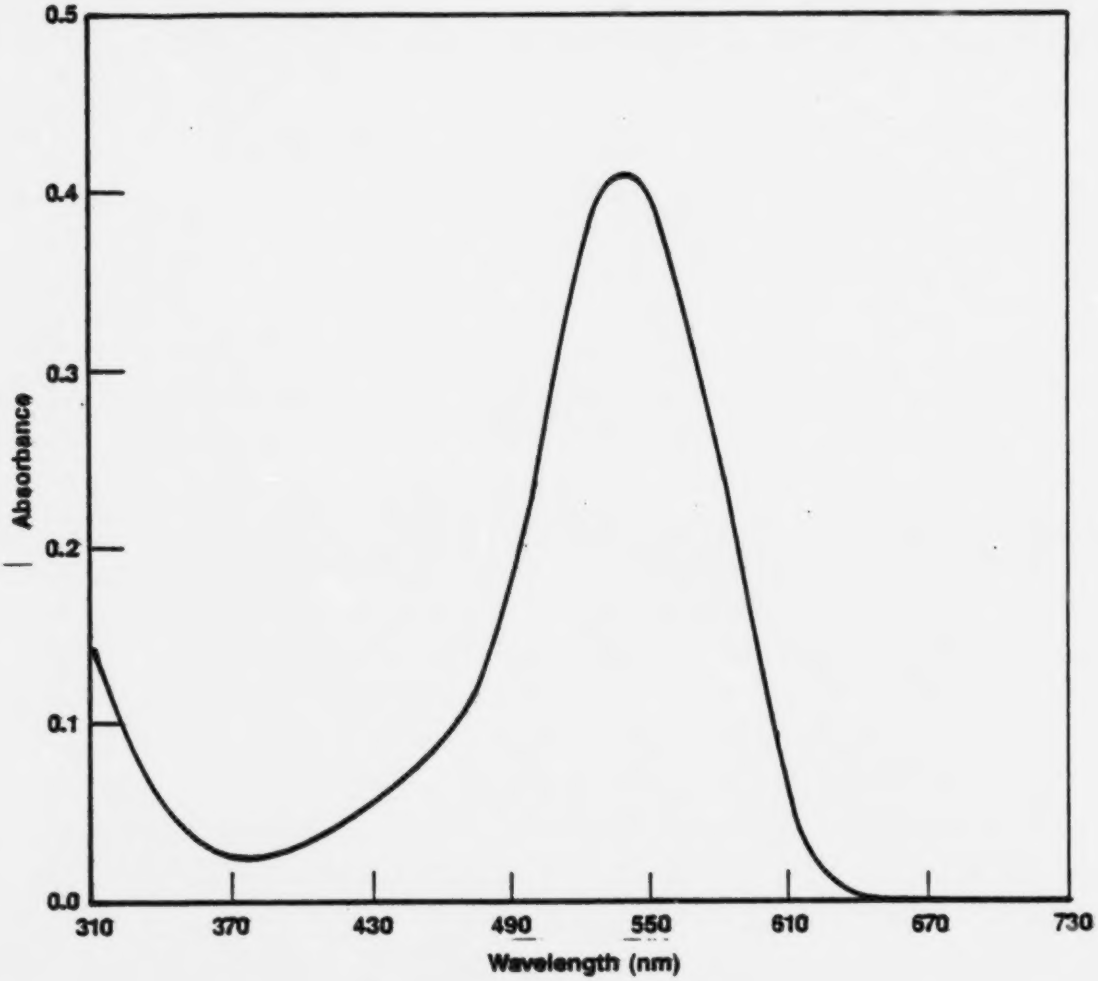


Figure 1. Absorption Spectrum for 0.5 mg/L Cr (VI) by Diphenylcarbazide Spectrophotometry

In acid solution, chromate and dichromate are readily reduced as shown in the following half reactions:

$$HCrO_4^- + 7H^+ + 3e^- \longleftrightarrow Cr^{3+} + 4H_2O \qquad E^o = 1.195V$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longleftrightarrow 2Cr^{3+} + 7H_2O \qquad E^o = 1.33V$$

The Nernst Equation for the $Cr_2O_7^{2-}/Cr^{3+}$ couple indicates a large dependency of this half reaction on $[H^+]$, reduction of Cr(VI) is therefore thermodynamically favored at low pH. At near neutral and alkaline pH, the latent or solubilized $Cr(OH)_3$ can participate in an oxidation reaction, yielding Cr(VI) as CrO_4^{2-}, as shown below:

$$Cr(OH)_{3(hyd)} + 5OH^- \longleftrightarrow CrO_4^{2-} + 4H_2O + 3e^- \qquad E^o = -0.13V$$

The electrode potential indicates that Cr^{3+} should be easily oxidized and CrO_4^{2-} should be stable at alkaline pH, but the rate of oxidation of trivalent chromium may be limited by the rate of solubilization of $Cr(OH)_{3(S)}$.

In phase II and phase III testing, analytical results have been presented on many aspects of the Cr(III)-Cr(VI) redox couple considered critical for handling, digestions, and measurements of Cr(VI) in solid waste samples. These results were obtained with synthetic aqueous sample solutions and with digestions of Cr(III) and Cr(VI) compounds. Special emphasis was placed on documenting Cr(VI) reduction by sulfide under various pH conditions in simulated aqueous samples. Extensive testing was also performed to determine the ability of the three digestion methods to (1) solubilize insoluble chromates and (2) provide a stable redox environment for Cr(III) and Cr(VI), in the presence of added oxidants and reductants. Simulated aqueous wastes were also employed to determine potential reduction of Cr(VI) during sample digest filtrations and potential DPC spectrophotometric interferences due to residual acid following nitric acid digestions.

The nitric acid/persulfate digestion method was eliminated from further consideration during the phase III testing. The two remaining digestion methods, an alkaline digestion and a nitric acid digestion, were applied to authentic environmental samples in phase IV.

For the alkaline digestion method, the percent recovery of aqueous Cr(VI) spikes and the percent oxidation of aqueous Cr(III) spikes were determined by DPC spectrophotometry for each sample. The total concentration of chromium in the sample digest solutions was determined independently by inductively coupled plasma-optical emission spectrometry (ICP-OES). For each sample carried through the alkaline digestion procedure, the chemistry of endogenous chromium in the sample was inferred from the results based on aqueous Cr(III) and Cr(VI) spikes.

Results are presented for three environmental samples carried through the nitric acid digestion procedure. Samples were spiked and analyzed as with the alkaline digestion procedure. Similar inferences about the chemistry of endogenous chromium in the sample were based on results for aqueous Cr(III) and Cr(VI) spikes.

SECTION 2

CONCLUSIONS

Phase I research activities demonstrated that the EPA protocol for SW-846 Method 7196 (Diphenylcarbazide Spectrophotometry) provides a sensitive method for Cr(VI) determinations in aqueous solution. Instrument response was linear over two orders of magnitude of Cr(VI) concentration (0.01 to 1.0 mg/L). The method was specific for Cr(VI) in the presence of at least 1000-fold excess of Cr(III).

Phase II research activities addressed the stability of Cr(VI) in aqueous solutions containing Cr(III) and sulfide as a function of pH. In alkaline solutions, reduction of Cr(VI) to Cr(III) by sulfide was slow. As predicted by standard electrochemical potentials, the reduction of Cr(VI) was increased in acidic solutions. These results have two significant ramifications: (1) environmental samples for Cr(VI) analyses should not be preserved by acidification to pH 2 and (2) diphenylcarbazide reagent should be added to an alkaline sample before pH adjustment to 2 with sulfuric acid to minimize Cr(VI) reduction in the quantification step; this verifies proper order of addition of the two reagents as described in Method 7196.

Phase III research activities demonstrated that a digestion medium consisting of 50 percent (v/v) nitric acid and 5 percent (w/v) potassium persulfate is not satisfactory for digestions of solid samples prior to Cr(VI) determinations. Hexavalent chromium was reduced by the digestion medium despite the presence of potassium persulfate, generally considered a strong oxidizing compound. At nitric acid concentrations of 20 percent or less, the nitric acid/persulfate medium demonstrated oxidizing properties.

The 50 percent nitric acid medium (without persulfate) and the alkaline medium (2 percent sodium hydroxide/3 percent sodium carbonate) both successfully solubilized insoluble barium chromate. Furthermore, the valence states of trivalent and hexavalent chromium were maintained for standard solutions carried through either digestion procedure. However, in the presence of oxidizing or reducing agents, the valence states of chromium species were not maintained in either digestion medium; the extent of valence state conversion was dependent on the concentration of the specific oxidant or reductant added.

Phase IV research activities focused on evaluating the ability of the

50 percent nitric acid medium and the alkaline medium to maintain the valence states of chromium during digestions of authentic environmental samples. Eight solid samples were analyzed for Cr(VI) by DPC spectrophotometry following alkaline digestions. Complete recoveries of Cr(VI) spikes were obtained in alkaline media by the DPC method for most samples (5 out of 8); Cr(VI) spikes were reduced in Municipal Digested Sludge (organic matrix), Tannery Sludge "B" (organic/sulfide matrix), and NBS-SRM 1646 Estuarine Sediment. Partial oxidation of Cr(III) spikes was obtained in alkaline media for many of the samples (4 out of 8); Cr(III) spikes were stable in Electroplating Sludge, Tannery Sludge "B" (organic/sulfide matrix), NBS-SRM 1646 Estuarine Sediment, and Municipal Digested Sludge. Partial oxidation of Cr(III) spikes in alkaline media produced measurement errors in Cr(VI) concentration by as much as 100 percent (positive bias).

Of the eight solid samples, only the electroplating sludge sample was successfully analyzed for Cr(VI) using an alkaline digestion and DPC spectrophotometry. Although unconfirmed by a collaborative method, endogenous Cr(VI) in the electroplating sludge was measured as determined by spike recovery data; Cr(VI) spikes were completely recovered and no measurable oxidation was observed.

Three solid samples were digested in the 50 percent nitric acid medium and analyzed by DPC spectrophotometry. Although no oxidation of Cr(III) spikes was observed in any of the samples, Cr(VI) spikes were completely reduced in all three samples.

DPC spectrophotometry was limited by color interferences encountered in many environmental samples. The interferences ranged from turbidity and color formation before the addition of DPC to turbidity and color formation after DPC addition. Turbidity and color interference was minimized whenever possible by dilution but this often led to high imprecision.

RECOMMENDATIONS

From the compiled data and observations made during this research task, certain recommendations are suggested for future research work and to the feasibility of speciation analysis of insoluble chromium compounds. These recommendations are as follows:

1. Use of the alkaline digestion, Method 3060, for chromium speciation analysis of solid samples is not recommended. Slightly soluble trivalent chromium can be partially oxidized while hexavalent chromium can be slowly reduced.

2. Discontinue further research into developing a digestion procedure for chromium speciation of solid samples. The stability of the chromium oxidation state once solubilized in either acid or base media is matrice dependent and cannot be predicted in environmental samples.

3. Modify Method 7196 for improved sensitivity for the analysis of hexavalent chromium in the dissolved fraction of ground and surface waters.

4. Develop a hybrid technique involving ion chromatographic separations of hexavalent and trivalent chromium combined with on-line ultra-sensitive detection of the individual chromium species. Recent advances in ion chromatography should provide a low cost analytical means for speciating the dissolved fraction of chromium in ground and surface waters.

SECTION 4
MATERIALS AND METHODS

INSTRUMENTATION

Diphenylcarbazide Spectrophotometry - Method 7196

Hexavalent chromium measurements were performed by DPC spectrophotometry (SW-846 Method 7196) using either a Beckman Model DU-2 or a Cary Model 14M spectrophotometer. Absorbances were measured at 540 nm using a matched set of 1-cm quartz rectangular cells. The Cary Model 14M spectrophotometer was also used for spectral scanning purposes.

In the DPC spectrophotometric method, a standard or sample aliquot was typically added to a 100-mL volumetric flask. Two mL of DPC reagent were added and mixed. Alkaline sample digest solutions were acidified with sulfuric acid to a pH of 2 +/- 0.5 and then diluted to calibrated volume with deionized water for color development. Acidic sample digest solutions with a pH less than 2 required no pH adjustment. Standard and sample absorbances were measured 10 to 15 minutes after initial color development except where stated otherwise in specific applications.

Deionized water served as the reference solution except where stated otherwise in specified applications. Small blank readings for deionized water, generally less than 0.006 absorbance unit, due to a slight difference in transmission properties and positioning of the sample and reference cells were subtracted from each of the measured absorbances. No detectable blank contribution due to residual Cr(VI) contamination in the spectrophotometric reagents was measured.

A linear calibration curve was constructed each day that test samples were analyzed. A reagent blank and three aqueous standard solutions containing 0.05, 0.50 and 0.75 mg/L of Cr(VI) were typically used for calibration. Calibration check standards were also analyzed periodically throughout the course of analyses to verify stability of the calibration curve.

Inductively Coupled Plasma - Optical Emission Spectrometry

Total chromium measurements on environmental samples were performed by inductively coupled plasma - optical emission spectrometry (ICP-OES) using a Jobin-Yvon Model 70P combination system. Emission intensities were measured under computer control using a fixed channel for chromium (205.55-nm ion line) on the Model 32 polychromator of the combined polychromator/monochromator optical system. The Model 32 polychromator, consisting of a 0.5-m focal length optical configuration with a 3600 grooves/mm holographic grating, was operated in an independent mode. The ICP-OES operating parameters are summarized in TABLE 1.

A linear calibration curve was constructed from a standard blank and an appropriate chromium standard solution within the linear range of the instrument. The aqueous calibration solutions were prepared using reagents to simulate the digest matrix of the diluted sample. Calibration check standards were analyzed periodically throughout the course of analyses to verify stability of the calibration curve.

pH and Redox Potentiometry

A standard pH meter (Orion Research, Inc.) and hydrogen electrode system was used for pH measurements. An apparatus for measuring redox potentials of simulated aqueous samples was assembled according to the manufacturer's (Orion Research, Inc.) instructions. The electrode unit was a Model 96-78 platinum redox electrode combined with a silver/silver chloride reference electrode in a single body which could be directly connected to the digital "ionanalyzer" meter. Proper operation of the electrode assembly was verified by performing potential measurements on two $K_4Fe(CN)_6 \cdot 3H_2O/K_3Fe(CN)_6$ solutions of different concentrations and of known potentials.

REAGENTS

Deionized water with a minimum electrical resistivity of 15 megaohm-cm (The Barnstead Company, Division of Sybron Corporation, Boston, MA) or equivalent; deionized water with a minimum electrical resistivity of 1 megaohm-

TABLE 1. SUMMARY OF ICP-OES OPERATING PARAMETERS FOR CHROMIUM

Radio Frequency (RF) Generator (PlasmaTherm) - 27.12 MHz

Forward Power (watts) - 1100
Reflected Power (watts) - 0

Torch (Fassel-type, 3 concentric glass tubes)

Argon Flow Rates (L/min)

Plasma (Coolant) Gas - 12
Auxiliary (Sheath) Gas - 0.8
Aerosol (Carrier) Gas - 0.7

Sample Delivery Rate

Peristaltic Pump (mL/min) - 1

Nebulizer (Meinhard-type, glass concentric)

Pressure (psi) - 32

Mass Flow Controller - 684

Observation Height (mm) - 7-10, above load coil

Signal Integration Period (sec) - 10

Number of Integrations - 3

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cm (Peck Water Systems Corporation, Canton, OH) or equivalent served as the inlet source for the Sybron/Barnstead deionization unit.

Barium chromate, $BaCrO_4$, FW 253.33; "Certified" reagent grade (Fisher Scientific Company, Fair Lawn, NJ) or equivalent.

Lead chromate, $PbCrO_4$, FW 323.18; ACS reagent grade (G. Frederick Smith Chemical Company, Columbus, OH) or equivalent.

Sodium carbonate, Na_2CO_3, anhydrous, FW 105.99; Analytical reagent grade (Mallinckrodt, Inc., Paris, KY) or equivalent.

Sodium hydroxide, NaOH, FW 40.00; "Baker Analyzed" reagent grade, (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Alkaline digestion solution, 2 percent (w/v) sodium hydroxide and 3 percent (w/v) sodium carbonate: Prepared by dissolving 20 g sodium hydroxide and 30 g sodium carbonate in 1 L of deionized water.

Sodium sulfide, $Na_2S \cdot 9H_2O$, FW 240.2; "Baker Analyzed" reagent grade, (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Potassium permanganate, $KMnO_4$, FW 158.04; "Baker Analyzed" ACS reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Potassium persulfate, $K_2S_2O_8$, FW 270.32; "Baker Instra-Analyzed" ACS reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Manganese dioxide, MnO_2, FW 86.94; 99+ percent (Aldrich Chemical Company, Inc., Milwaukee, WI) or equivalent.

L-Ascorbic acid, $C_6H_8O_6$, FW 176.12; Certified ACS reagent grade (Fisher Scientific Company, Fair Lawn, NJ) or equivalent.

Sym-diphenylcarbazide (2,2'-Diphenylcarbonic dihydrazide), FW 242.3 (Sigma Chemical Company, St. Louis, MO or equivalent); refrigerated when not in use.

Acetone, $(CH_3)_2CO$, FW 58.08; "Baker Analyzed" ACS reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Diphenylcarbazide solution, 0.5 percent (w/v): Prepared by dissolving 250 mg sym-diphenylcarbazide in 50 mL acetone.

Sulfuric acid, H_2SO_4, concentrated (96 percent, 36 normal), FW 98.08; Analytical reagent grade (Mallinckrodt, Inc., Paris, KY) or equivalent.

Sulfuric acid, 10 percent (v/v): Prepared by diluting 10 mL of concentrated sulfuric acid to 100 mL with deionized water.

Nitric acid, HNO_3, concentrated (70 percent, 16 normal), FW 63.0; "Baker Instra-analyzed" reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent.

Perchloric acid, $HClO_4$, concentrated (60 percent, FW 100.46; ACS reagent grade (G. Frederick Smith Chemical Company, Columbus, OH) or equivalent.

STANDARD SOLUTIONS

Hexavalent chromium: (1) commercial 1000 mg/L atomic absorption stock standard, potassium chromate, K_2CrO_4 (MCB Manufacturing Chemists, Inc., Cincinnati, OH) or equivalent, (2) commercial 1000 mg/L atomic absorption stock standard, potassium dichromate, $K_2Cr_2O_7$ (Fisher Scientific Company, Fair Lawn, NJ) or equivalent, and (3) potassium dichromate, $K_2Cr_2O_7$, FW 294.19; "Baker Analyzed" reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent: a 1000 mg/L stock standard solution was prepared by dissolving potassium dichromate in deionized water.

Trivalent chromium: chromium nitrate, $Cr(NO_3)_3 \cdot 9H_2O$, FW 400.15; "Baker Analyzed" reagent grade (J. T. Baker Chemical Company, Phillipsburg, NJ) or equivalent: a 1000 mg/L stock standard solution was prepared by dissolving chromium nitrate in deionized water.

ENVIRONMENTAL SAMPLES

River Sediment

The river sediment sample (NBS-SRM 1645) is a freeze-dried sediment prepared from material dredged from the bottom of the Indiana Harbor Canal near Gary, Indiana. The certified concentration for chromium in NBS-SRM 1645 is 2.96 percent with an uncertainty of 0.28 percent. The uncertainty represents the 95 percent tolerance limits for an individual sub-sample; i.e., 95 percent of the sub-samples from a unit of this SRM would be expected to have the certified chromium concentration within the indicated range of values 95 percent of the time. The chemical form of chromium in NBS-SRM 1645 is unknown.

The certified concentration of iron is 11.3 percent. The following values, although not certified, for additional matrix components were also provided: SiO_2 - 51 percent, MgO - 4 percent, Al_2O_3 - 4 percent, CaO - 4 percent, and phosphorus - 0.05 percent. These inorganic constituents represent approximately 75 weight percent of the total sediment material.

Municipal Digested Sludge

The municipal digested sludge sample is a freeze-dried water pollution quality control sludge material supplied from the inventory of the Environmental Protection Agency. The reference concentration for chromium in Municipal Digested Sludge (MDS), as determined by EPA reference laboratories, is 0.204 mg/g with an uncertainty of 0.090 mg/g at the 95 percent confidence level. The chemical form of chromium in Municipal Digested Sludge is unknown.

The sludge matrix is relatively high in organics including approximately 7 percent petroleum hydrocarbons and approximately 23 percent total organic carbon (TOC). The principal inorganic matrix components include approximately 0.5 percent aluminum, 0.1 percent copper, 2 percent iron, 1 percent zinc, and 2 percent titanium.

Contaminated Soils "A" and "B"

Contaminated soil samples "A" and "B" are milled soil samples. Both soil samples appeared to be freeze-dried. Soil samples "A" and "B" contain approximately 0.1 percent chromium and 1 percent chromium, respectively, as indicated from independent analyses records. The chemical form of chromium in Contaminated Soils "A" and "B" is unknown. Historical information on the sample matrices was not provided.

Electroplating Sludge

The electroplating sludge sample is a freeze-dried, quality control sludge material (WP-286) supplied from the inventory of the Environmental Protection Agency. The reference concentration for chromium in Electroplating Sludge, as determined by EPA reference laboratories, is approximately 7 mg/g on a dry-weight basis. The chemical form of chromium in Electroplating Sludge is unknown. Minimal information on the history of the sample was available although reference concentrations for selected metals were provided. The two principal quantified inorganic constituents, in addition to chromium, include aluminum, approximately 3.6 mg/g, and zinc, approximately 3.5 mg/g.

Estuarine Sediment

The estuarine sediment sample (NBS-SRM 1646) is a freeze-dried sediment dredged from the Chesapeake Bay. The certified concentration for chromium in NBS-SRM 1646 is 76 µg/g with an uncertainty of 3 µg/g. The estimated uncertainty represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods, and material variability for sample sizes of 500 mg or more. The chemical form of chromium in NBS-SRM 1646 is unknown.

The certified values for aluminum and iron are 6.25 percent and 3.35 percent, respectively. The following values, although not certified, for additional matrix components were provided: silicon - 31 percent, sodium - 2.0 percent, potassium - 1.4 percent, sulfur - 0.96 percent and titanium - 0.51 percent. These inorganic constituents represent approximately 45 weight percent of the total sediment material.

Tannery Sludges "A" and "B"

The tannery sludge samples represent chrome tanning sludges of low-sulfide content ("A") which had not undergone a hair removal process (no beamhouse) and of high-sulfide content ("B") which had undergone the full beamhouse process. The beamhouse process (hair removal) yields a lime-protein rich sludge with high sulfide from sodium sulfide additions. Based on analytical information submitted with the tanning sludge samples, the low-sulfide sludge was characterized as approximately 30-40 percent solids with a chromium concentration of approximately 25 mg/g. The high-sulfide sludge sample was a sludge of high moisture content reported to contain 15 percent solids and a chromium level of 39 mg/g. It was not verified whether the reported chromium concentration was based on a "dry-weight" or "wet-weight" basis. The chemical form of the chromium in these tannery sludge samples is unknown. Information on sulfide concentrations was not provided with the samples. Quantitative determinations of sulfide were not performed by Battelle to obtain this information.

River Water

Approximately 500 mL quantities of two river water samples were collected along the east bank of the Scioto River between the Marina and the Griggs Reservoir Dam on August 7, 1986, 8:30 a.m. The pH of the water samples was 8.3 within an hour of collection. The river water samples appeared slightly yellow in color with slight turbidity. The unfiltered water samples were digested and analyzed within 24 hours of collection. The chemical form of any endogenous chromium in the river water is unknown. No other sample history was available. The river water samples were collected in two acid-cleaned polyethylene bottles. Prior to collection of the samples used for analyses, the same polyethylene containers were rinsed with river water from the same location for conditioning purposes.

SECTION 5
EXPERIMENTAL PROCEDURES

SIMULATED SAMPLE ANALYSES

Selected digestion methods (alkaline, nitric acid and nitric acid/persulfate) were tested on simulated samples of barium chromate and trivalent chromium nitrate prior to their evaluations on authentic environmental samples. The digestion methods were tested on the simulated samples alone and in the presence of selected reducing and oxidizing species commonly encountered in the environment.

Alkaline Digestions (Method 3060)

Appropriate masses of simulated solid samples were digested in the alkaline medium (aqueous mixture of 2 percent sodium hydroxide and 3 percent sodium carbonate) according to procedure. Because the pressure-filtration step was very lengthy, the procedure was slightly modified after initial trials by replacing the pressure-filtration apparatus with a Millipore glass vacuum-filtration system. The vacuum-filtration apparatus including a 47-mm diameter filter membranes having average pore porosities of 0.45 µm.

Nitric Acid Digestions

Appropriate masses of simulated solid samples were digested in a 50 percent nitric acid medium. One hundred-mL of deionized water were first added to test portions of the solid samples prior to the addition of 100 mL of concentrated nitric acid. The concentrated nitric acid was slowly added in small volumetric increments under controlled stirring and heating conditions. The test samples were digested on a hot plate at low heat for approximately 2 hours and then vacuum-filtered through 0.45-µm filter membranes according to the procedure of Method 3060. The filtrates were then transferred to 1-L volumetric flasks and diluted to calibrated volume with deionized water.

Nitric Acid/Persulfate Digestions

Appropriate masses of simulated samples were digested in a nitric acid/persulfate medium consisting of 50 percent (v/v) nitric acid and 5 percent (w/v) potassium persulfate. The potential feasibility of such a digestion medium was predicated on the possibility of maintaining a highly oxidizing medium with potassium persulfate in the digestion solution to keep Cr(VI) in an oxidized state even under extremely acidic conditions.

ENVIRONMENTAL SAMPLE ANALYSES

The eight solid samples and one liquid sample were analyzed for total chromium concentrations by ICP-OES. Independent sample digestion methods were used: nitric acid - perchloric acid digestions for the eight solid samples and nitric acid digestions for the river water sample. These analyses were performed prior to hexavalent chromium analyses to determine total chromium concentrations in the environmental samples using rigorous digestion methods; the total chromium concentrations were used to estimate Cr(VI) and Cr(III) spike concentration levels in the hexavalent chromium experiments.

The nine environmental samples were analyzed for hexavalent chromium using an alkaline digestion and quantification by DPC spectrophotometry; three of the solid samples were also analyzed for hexavalent chromium using a mild nitric acid digestion. All sample digest solutions were also analyzed for total chromium concentrations by ICP-OES to provide information on the relative solubilities of chromium species in alkaline and nitric acid digestion media.

Except for the two tannery sludge samples, the environmental samples were digested and analyzed as received. Preliminary sample preparation of the tannery sludges included an attempt to partially homogenize the moist bulk samples with respect to moisture content. Approximately 250 g of each sludge sample was transferred to an acid-cleaned 500-mL plastic bottle and stirred for 5 minutes with a ceramic spoon. The "homogenized" sub-samples were stored in a refrigerator until sampling for analyses was required. After a homogenized sub-sample was removed from the refrigerator and warmed to room temperature for sampling, the tannery sludge sub-sample was stirred again with a ceramic spoon prior to taking test portions for analyses.

Nitric Acid - Perchloric Acid Digestions

Prior to hexavalent chromium analyses, total chromium concentrations were determined in the eight solid environmental samples using an independent digestion method and quantification by ICP-OES. One-gram test portions of the solid samples were initially digested in 20 mL of 50 percent nitric acid. After the addition of 10 mL of concentrated perchloric acid, each sample solution was further digested until dense perchloric acid fumes appeared. Heating of each sample was continued until slightly less than 10 mL of digest solution remained. The digest solutions were gravity-filtered, with deionized water rinsing, into 100-mL volumetric flasks and diluted to calibrated volume for ICP-OES analyses.

Calibration for ICP-OES analyses of the solid environmental samples was performed using a standard blank and a 10 mg/L chromium standard solution. The standard blank and calibration standard solutions were prepared in 10 percent (v/v) perchloric acid to approximate the matrix acid and concentration of the sample digest solutions.

A rigorous nitric acid digestion without perchloric acid was used as an alternate digestion method for total chromium measurements of river water samples. Duplicate 30-mL aliquots of river water were digested in 30 mL of acid medium (50 percent nitric acid) in a 100-mL beaker on a hot plate with stirring for 2 hours. The river water samples were digested at a temperature of 80^{o}C +/- 10^{o}C. The sample digest solutions were vacuum-filtered through 0.45-um filters, collected in 100-mL volumetric flasks and diluted to calibrated volume with deionized water. A reagent blank was also carried through the same digestion procedure and analyzed with the samples. Calibration for ICP-OES analyses of river water samples was performed using a standard blank and a chromium standard solution within the linear range of the instrument; the standard blank and standard solutions contained the same amount of nitric acid as the digested sample solutions. Control check standards were also analyzed to verify stability of the calibration curve during sample analyses.

Alkaline Digestions (Method 3060)

Hexavalent and total chromium concentrations were determined in alkaline digest solutions of the nine environmental samples by DPC spectrophotometry and ICP-OES, respectively. One-gram test portions of the eight environmental samples were digested in 50 mL of the alkaline medium (an aqueous mixture of 2 percent sodium hydroxide and 3 percent sodium carbonate), except where stated otherwise, in a 100-mL beaker on a hot plate with stirring for approximately 45 minutes. The sample solutions were heated to a temperature of 80°C +/- 10°C. After a cooling period, the sample digest solutions were then vacuum-filtered through a 47-mm filter membrane (0.45-um pore size) of a glass Millipore filtering apparatus, transferred into 100-mL volumetric flasks and diluted to near calibrated volume with deionized water. After addition of concentrated nitric acid to adjust the pH to approximately 7, each sample solution was diluted to calibrated volume with deionized water.

Fifteen-mL aliquots of the river water sample were digested in 15 mL of alkaline digestion medium as described above for the solid samples. Because of the low endogenous chromium concentration in the river sample, each filtrate was diluted to a final volume of 50 mL to maintain a minimal dilution factor. Two sets of the alkaline digestions were performed for quantification by DPC spectrophotometry and ICP-OES. For the DPC spectrophotometric measurements, color development was performed in the 50-mL volumetric flasks for collection of the sample filtrates to alleviate further dilution. The additional set of sample filtrates diluted to 50 mL were analyzed directly for total chromium by ICP-OES. On this basis, the ICP-OES measurements would be directly comparable to the DPC spectrophotometric measurements for the samples within the same sample sets.

Calibration for ICP-OES analyses was performed using a standard blank and a chromium standard solution within the linear calibration region of the instrument. The standard blank and calibration standard solutions were prepared in an alkaline digest matrix equivalent to the final matrix of the diluted samples; the pH of the alkaline matrix solution was neutralized with concentrated nitric acid followed by further acidification to pH 2 with sulfuric acid.

Nitric Acid Digestions

Hexavalent and total chromium concentrations were determined in nitric acid digest solutions of three solid samples (River Sediment, Municipal Digested Sludge, and Contaminated Soil "A") by DPC spectrophotometry and ICP-OES, respectively. One-gram test portions of the three environmental samples were digested in 50 mL of acid medium (50 percent nitric acid) in a 100-mL beaker on a hot plate with stirring for 2 hours. The samples were digested at a temperature of 80°C +/- 10°C. The sample digest solutions were vacuum-filtered through 0.45-µm filter membranes of a glass Millipore filtering apparatus, transferred into 100-mL volumetric flasks and diluted to calibrated volume with deionized water.

DILUTION SCHEMES FOR ENVIRONMENTAL SAMPLE ANALYSES

Various dilution schemes required for DPC spectrophotometric and ICP-OES analyses of the nine environmental samples due to a wide range of endogenous chromium concentrations in the samples. The dilution schemes for analyses of the environmental samples following alkaline and nitric acid digestions are summarized in TABLES 2 and 3, respectively.

CHROMIUM SPIKING SCHEMES FOR ENVIRONMENTAL SAMPLE ANALYSES

Pre-Digestion Spikes

The redox behavior of Cr(VI) and Cr(III) during digestions of environmental samples was evaluated by a series of pre-digestion chromium spiking experiments. Six 1-gram test portions of solid samples and 15-mL test aliquots of river water were used to form three sets for testing of each environmental sample: (1) duplicate unspiked samples, (2) duplicate samples spiked with Cr(III), and (3) duplicate samples spiked with Cr(VI). The concentrations of the Cr(III) and Cr(VI) spikes were similar to the total endogenous chromium concentrations measured by ICP-OES following the independent digestion methods. Each chromium spike was added to the environmental sample prior to addition of the digestion media.

TABLE 2. SUMMARY OF DILUTION SCHEMES FOR ENVIRONMENTAL SAMPLE ANALYSES BY DPC SPECTROPHOTOMETRY AND ICP-OES FOLLOWING ALKALINE DIGESTIONS

Sample	Digestion (Sample/Medium)	Final Filtrate Volume (mL)	Filtrate Dilution[(a)] DPC	Filtrate Dilution[(a)] ICP
River Sediment	1 g/400 mL	1000	20X 100X(b)	None
Municipal Digested Sludge	1 g/50 mL	100	10X	10X
Contaminated Soil "A"	1 g/50 mL	100	50X	None
Contaminated Soil "B"	1 g/50 mL	100	100X	2.5X 10X(b)
Electroplating Sludge	1 g/50 mL	100	100X	2.5X 10X(b)
Estuarine Sediment	1 g/50 mL	100	1.43X	None
Tannery Sludge "A"	1 g/50 mL	100	100X	2X
Tannery Sludge "B"	1 g/50 mL	100	20X 100X(b)	10X
River Water	30 mL/30 mL 15 mL/15 mL	100 50	None --	-- None

(a) Dilution of digest filtrate of unspiked, Cr(III)-spiked, and Cr(VI)-spiked samples except where noted otherwise.

(b) Dilution of digest filtrate of Cr(VI)-spiked sample.

TABLE 3. SUMMARY OF DILUTION SCHEMES FOR ENVIRONMENTAL SAMPLE ANALYSES BY DPC SPECTROPHOTOMETRY AND ICP-OES FOLLOWING NITRIC ACID DIGESTIONS

Sample	Digestion (Sample/Medium)	Final Filtrate Volume (mL)	Filtrate Dilution[a] DPC	ICP
River Sediment	1 g/50 mL	1000	10X	None
Municipal Digested Sludge	1 g/50 mL	100	10X	None
Contaminated Soil "A"	1 g/50 mL	100	50X	None

(a) Dilution of digest filtrate of unspiked, Cr(III)-spiked, and Cr(VI)-spiked samples.

Hexavalent chromium spikes were added to the environmental samples in the form of aliquots of a chromium standard solution prepared by dissolving solid $K_2Cr_2O_7$ in deionized water. Trivalent chromium spikes were added to the environmental samples in the form of aliquots of a chromium standard solution prepared by dissolving solid $Cr(NO_3)_3 \cdot 9H_2O$ in deionized water. The pre-digestion chromium spiking manipulations applicable to the environmental sample analyses are summarized in TABLE 4.

Post-Digestion Spikes

The presence of multiplicative interferences in the quantification steps by DPC spectrophotometry or ICP-OES was checked by post-digestion spikes. Post-digestion spikes would differentiate between multiplicative interferences which altered the slope of the calibration curve during the quantification step and incomplete recoveries of pre-digestion chromium spikes. The post-digestion chromium spiking manipulations applicable to the environmental sample analyses are summarized in TABLE 5.

TABLE 4. SUMMARY OF PRE-DIGESTION CHROMIUM SPIKING SCHEMES FOR ENVIRONMENTAL SAMPLE ANALYSES

Sample(a)	Spike Addition	Standard Concentration(b,c)	Aliquot Added
River Sediment	30 mg	3 mg/mL	10 mL
Municipal Digested Sludge	0.2 mg	0.2 mg/mL	1 mL
Contaminated Soil "A"	1.0 mg	1.0 mg/mL	1 mL
Contaminated Soil "B"	8.5 mg	8.5 mg/mL	1 mL
Electroplating Sludge	8.5 mg	8.5 mg/mL	1 mL
Estuarine Sediment	76 ug	76 ug/mL	1 mL
Tannery Sludge "A"	5.7 mg	5.7 mg/mL	1 mL
Tannery Sludge "B"	7.8 mg	7.8 mg/mL	1 mL
River Water (30 mL)	50 ug	50 ug/mL	1 mL
River Water (15 mL)	25 ug	50 ug/mL	0.5 mL

(a) 1-g test portions of solid samples; 30-mL or 15-mL test aliquots of water sample.

(b) Cr(III) aqueous spiking solution prepared from solid $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in deionized water.

(c) Cr(VI) aqueous spiking solution prepared from solid $K_2Cr_2O_7$ dissolved in deionized water.

TABLE 5. SUMMARY OF POST-DIGESTION CHROMIUM SPIKING SCHEMES FOR ENVIRONMENTAL SAMPLE ANALYSES AFTER ALKALINE DIGESTIONS

Sample	Cr(VI) Spike Concentration (mg/mL)(a)	
	DPC	ICP
River Sediment	--	--
Municipal Digested Sludge	--	--
Contaminated Soil "A"	--(b)	--
Contaminated Soil "B"	0.5	1.0
Electroplating Sludge	0.5	1.0
Estuarine Sediment	0.76	0.76
Tannery Sludge "A"	0.5	1.0
Tannery Sludge "B"	0.5	2.0
River Water	--	0.5

(a) Cr(VI) spike concentration in final dilution of alkaline digest solution presented to the instrument for analysis.

(b) Cr(VI) spike concentration of 0.5 mg/L in final dilution of nitric acid digest presented to the instrument for analysis.

SECTION 6

RESULTS AND DISCUSSION

PHASE I - CHARACTERIZATION AND RUGGEDNESS EVALUATION OF DIPHENYLCARBAZIDE SPECTROPHOTOMETRY

Parameter and ruggedness evaluations of the EPA protocol for SW-846 Method 7196 were initially performed to test the feasibility of using Method 7196 as a probe for monitoring chromium redox phenomena during digestions and analyses of solid chromate materials and environmental samples. Concentration figures-of-merit for hexavalent chromium were determined and selected ruggedness parameters were tested using Method 7196.

Detection Limit

The detection limit (C_L) for Cr(VI) using Method 7196 was estimated by extrapolation from measured analyte concentrations to an analyte concentration with a signal-to-noise ratio of 3 using the equation recommended by the International Union of Pure and Applied Chemistry (IUPAC)[9]:

$$C_L = (1/m)\ k\ N_{rms}$$

where k is an arbitrary confidence factor, N_{rms} represents the root-mean-square (standard deviation) noise, and m is the slope of the calibration curve. A confidence factor of 3 for k is used to comply with the IUPAC criterion. The root-mean-square noise is estimated by the standard deviation of the absorbance measured for seven replicate 0.01 mg/L Cr(VI) standard solutions prepared and analyzed on a single day; 0.0005 absorbance unit is a representative value for the root-mean-square noise. A slope of 0.82 absorbance per mg/L is a representative value for m. Substitution of these values into equation (1) gives a detection limit of approximately 0.002 mg/L Cr(VI). This detection limit also corresponds to the concentration value calculated for the method detection limit (MDL)[10]. However, practical detectability of the given spectrophotometers with analog meter readouts, limited by readout error of the meter needle (uncertainty of approximately 0.002 absorbance unit), is approximately 0.01 mg/L Cr(VI). Detectability may be increased, if necessary, by using larger path-lenth absorption cells.

Linear Dynamic Range

The optimal range of calibration standards for Cr(VI) as dichromate and chromate was established using Method 7196. The experiments were conducted on different days to estimate day-to-day variability in the calibration curve.

The absorbances, corrected for DPC blanks, for a series of Cr(VI) standard solutions, ranging from 0.01 mg/L to 1.5 mg/L, are presented in TABLE 6. Absorbance measurements were performed on the Beckman Model DU-2 spectrophotometer except for the absorbance data in parentheses which were obtained on the Cary Model 14M spectrophotometer. No detectable blank contribution due to Cr(VI) contamination in the reagents or glassware was observed. Linearity was observed over a 100-fold concentration range from the detection limit, 0.01 mg/L, to approximately 1 mg/L.

The absorbance data in TABLE 6 were statistically examined with a linear regression algorithm using a hand calculator. The sensitivity (slope), intercept, and correlation coefficient were calculated for Cr(VI), as dichromate and chromate, on different days. An average slope of 0.82 absorbance per mg/L was obtained. Excellent day-to-day reproducibility of the calibration curve was achieved. No systematic uncertainty is introduced when either dichromate or chromate is used as the primary stock solution for Cr(VI).

Typical absorbance data for Cr(VI), as dichromate, are graphically presented in Figures 2 and 3. The lower concentration or absorbance range is presented in Figure 2 and the higher concentration or absorbance range is presented in Figure 3. The constructed lines in Figures 2 and 3 represent the linear regression fit ($r = 0.9999$) for 12 data points between 0.01 mg/L and 1.0 mg/L, inclusively.

A second set of typical calibration absorbance data for Cr(VI) as dichromate and chromate, measured over approximately a 100-fold concentration range on different days, were compiled. An average slope of 0.83 +/- 0.008 absorbance per mg/L was obtained for Cr(VI) as dichromate on six different days with a day-to-day variability of 1.0 percent. The average slope of the calibration curves for Cr(VI) as chromate on two different days was 0.84 +/- 0.006 absorbance per mg/L with a relative reproducibility of approximately 0.8 percent.

In all cases, correlation coefficients of the linear regressions for the individual calibration curves were between 0.9994 and 0.9999. The data

TABLE 6. CALIBRATION DATA FOR Cr(VI) AS DICHROMATE AND CHROMATE

Cr(VI) Concentration (mg/L)	Absorbance[a]			
	$K_2Cr_2O_7$		K_2CrO_4	
	#1	#2	#1	#2
0.010	---	(0.007)	0.011	0.010
0.020	0.015	---	---	---
0.025	---	0.021	(0.022)	(0.022)
0.050	0.040	(0.040)	(0.044)	(0.043)
0.075	---	(0.062)	0.064	0.064
0.10	0.082	(0.082)	0.085	0.085
0.15	0.125	---	---	---
0.20	0.165	---	---	---
0.25	---	0.209	0.207	0.214
0.50	0.406	(0.404)	(0.403)	(0.423)
0.75	---	0.616	0.608	0.626
1.0	(0.814)	0.815	0.805	0.813
1.5	1.14	---	---	1.15
Linear Regression				
No. Data Points	7	9	9	9
Slope (Abs/mg/L)	0.81	0.82	0.80	0.82
Intercept (Abs)	0.001	0.000	0.004	0.004
Corr. Coeff.	0.9999	0.9999	0.9999	0.9998

(a) Absorbances measured on Beckman Model DU-2; absorbances in parentheses measured on Cary Model 14M.

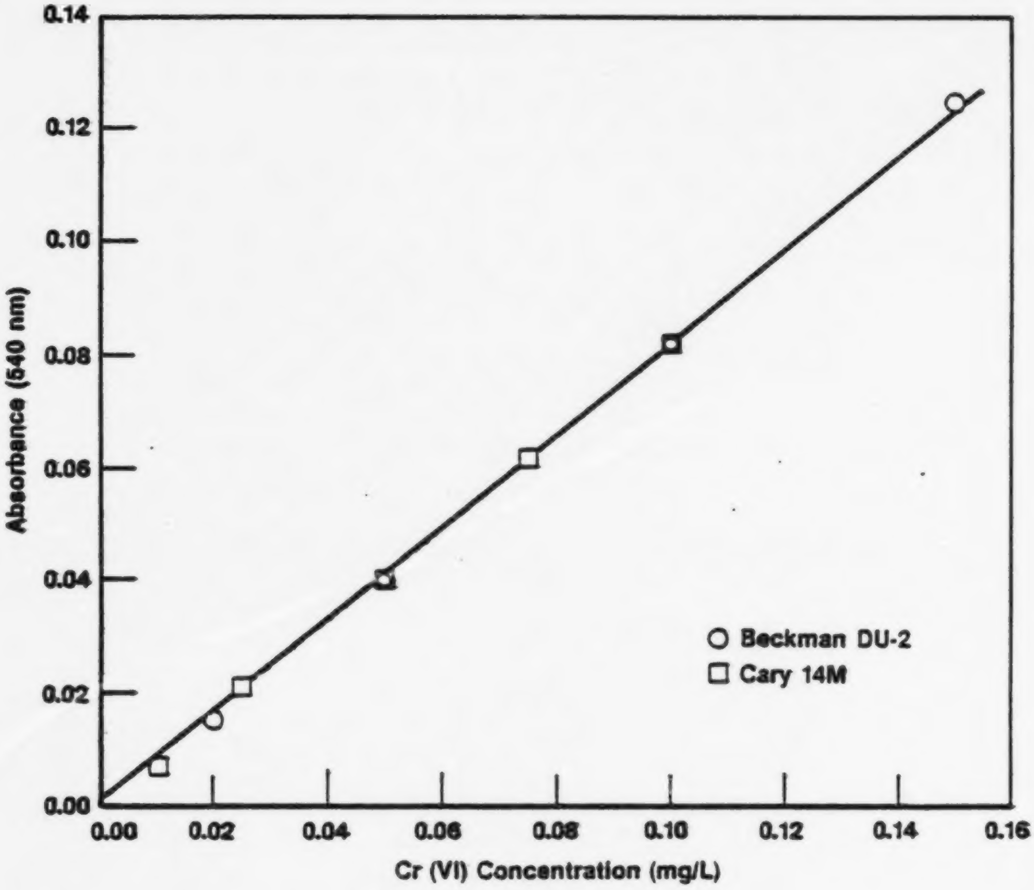

Figure 2. Calibration Curve for Cr (VI) as Dichromate in Low Absorbance Range

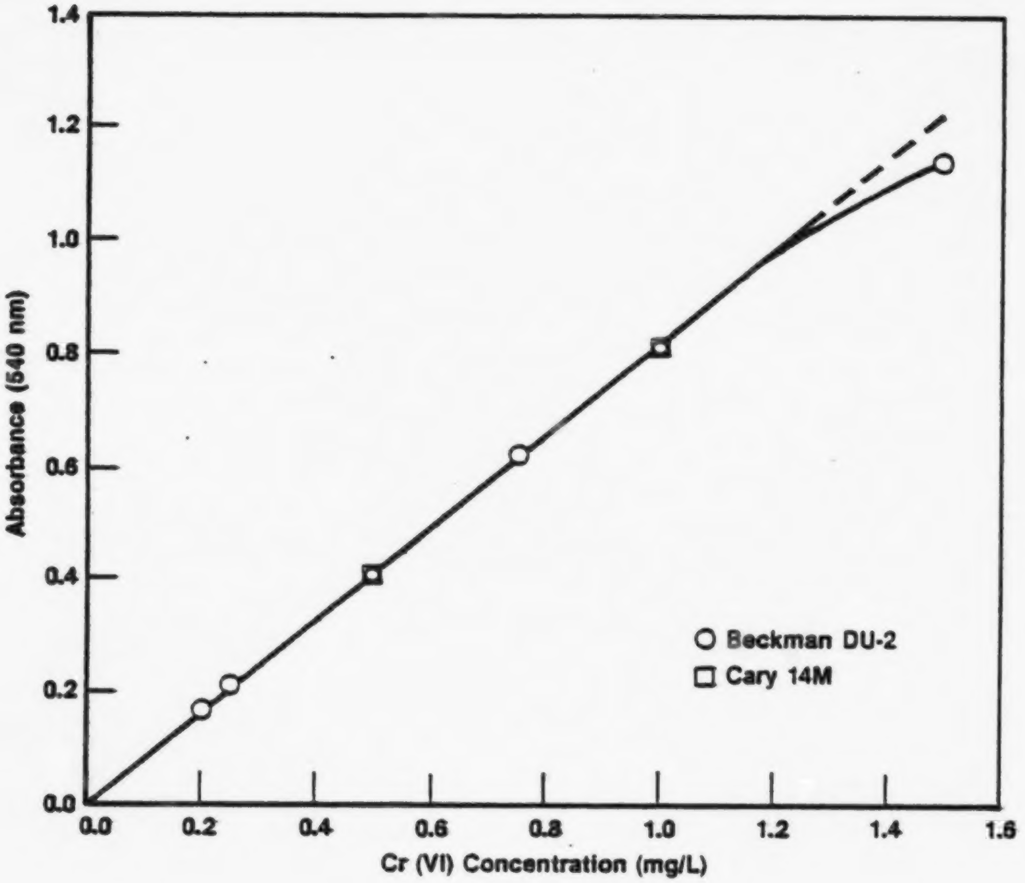

Figure 3. Calibration Curve for Cr (VI) as Dichromate in High Absorbance Range

indicated that the linear dynamic range of the method is sufficient to permit measurements of Cr(VI) concentrations at the 0.05 mg/L and 0.5 mg/L levels using the same instrument parameters and conditions.

Precision

The repeatability of Method 7196 was assessed by consecutive measurements of the absorbances of seven solutions of Cr(VI) as dichromate at the 0.01 mg/L, 0.05 mg/L, and 0.5 mg/L concentrations. The data from each set of measurements, repeated on separate days, are presented in TABLE 7. The average repeatability (reported as percent relative standard deviation) for the two days was 5.7 percent at the 0.01 mg/L level, 1.6 percent at the 0.05 mg/L level, and 0.41 percent at the 0.5 mg/L level.

The day-to-day variability of measurements for Cr(VI) as dichromate at three concentrations was examined. Each Cr(VI) concentration was measured on a minimum of 11 different days. The data for the three Cr(VI) concentrations are presented in TABLE 8. The day-to-day variability was 2.5 percent for 0.05 mg/L, 1.2 percent for 0.5 mg/L, and 0.95 percent for 1 mg/L. These precision data indicate that the repeatability and day-to-day variability of DPC spectrophotometric measurements in deionized water using Method 7196 are excellent over the relevant concentration range for Cr(VI).

Time Stability of the Cr(III)-DPCO Complex

The absorbances of a reagent blank and eight standard solutions, extending from 0.01 mg/L to 1 mg/L, were monitored for 90 to 120 minutes after color development. No color degradations were observed for any of the solutions for the first 90 minutes. Standards with less than 0.50 mg/L Cr(VI) were monitored for an additional 30 minutes; the measured absorbances remained constant throughout the test period. The data is summarized in TABLE 9.

This experiment verified that sample dilutions could be made to contain as much as 1 mg/L Cr(VI) using the adopted test procedure. The red-violet color developed in the solutions is stable for at least 90 minutes in a deionized water matrix. However, the present data do not preclude complications which may occur in the presence of redox agents and other metals in environmental samples.

TABLE 7. REPEATABILITY OF MEASUREMENTS FOR Cr(VI) AS DICHROMATE AT SELECTED CONCENTRATIONS

	Absorbance					
	0.01 mg/L Cr(VI)		0.05 mg/L Cr(VI)		0.5 mg/L Cr(VI)	
	#1	#2	#1	#2	#1	#2
	0.009	0.007	0.040	0.042	0.413	0.412
	0.008	0.007	0.040	0.042	0.411	0.413
	0.009	0.008	0.040	0.042	0.416	0.415
	0.009	0.007	0.041	0.042	0.411	0.415
	0.009	0.008	0.040	0.044	0.416	0.412
	0.009	0.008	0.041	0.042	0.413	0.413
	0.009	0.007	0.041	0.042	0.412	0.412
Average	0.009	0.007	0.040	0.042	0.413	0.413
Std. Dev.	0.0004	0.0005	0.0005	0.0008	0.0021	0.0013
Rel. Std. Dev.	4.4%	7.1%	1.3%	1.9%	0.51%	0.31%

TABLE 8. DAY-TO-DAY VARIABILITY OF MEASUREMENTS FOR Cr(VI) AS DICHROMATE AT SELECTED CONCENTRATIONS

Cr(VI) Concentration mg/L	Number of Data Points	Absorbance Average	RSD Percent
0.05	11	0.043	2.5
0.5	15	0.428	1.2
1	11	0.844	0.95

TABLE 9. TIME STABILITY OF THE Cr(III)-DPCO COMPLEX

Conc. mg/L	Time Hrs	ABS	Time Hrs	ABS	Time Hrs	ABS	Time Hrs	ABS
0.00	0.167	-0.003	0.530	-0.004	1.18	-0.003	1.95	-0.003
0.01	0.183	0.006	0.530	0.006	1.20	0.006	1.93	0.008
0.05	0.167	0.040	0.520	0.041	1.35	0.042	1.93	0.041
0.10	0.200	0.087	0.560	0.085	1.40	0.084	1.98	0.086
0.50	0.217	0.430	0.550	0.428	1.38	0.429	2.05	0.425
0.70	0.183	0.597	0.783	0.598	1.45	0.597	--	--
0.80	0.333	0.685	0.767	0.685	1.42	0.684	--	--
0.90	0.333	0.764	0.750	0.767	1.38	0.761	--	--
1.00	0.367	0.845	0.600	0.845	1.42	0.835	--	--

Specificity

Experiments were performed to verify the specificity of DPC spectrophotometry for Cr(VI) in the presence of high concentrations of Cr(III). These specificity tests required preliminary determinations of: (1) the spectral background absorbance at 540 nm due to the chromophoric property of aqueous Cr(III) and (2) the quantification of Cr(VI) contamination in the chromium nitrate salt used for Cr(III) spike solutions for this and subsequent experiments.

An absorption spectrum (310 nm to 730 nm) for a 00 mg/L Cr(III) test solution is presented in Figure 4. This test solution contains DPC reagent and has been adjusted to pH 2 with sulfuric acid. As shown in Figure 4, the 540-nm wavelength for DPC spectrophotometry lies on the shoulder of an absorption band for Cr(III) centered at approximately 580 nm.

Cr(VI) contamination in the chromium nitrate salt was determined by measuring the absorbances for two different 500 mg/L Cr(III) solutions at 540 nm. The first solution was pH-adjusted to 2 without the addition of DPC. Any measured absorbance from this solution would be due solely to background absorbance resulting from the chromophoric property of aqueous Cr(III). The second solution was prepared with the addition of DPC and pH adjustment to 2. The measured absorbance from this solution represented the sum of Cr(III) background absorbance and absorbance due to reaction of Cr(VI) contaminant with DPC reagent.

The results of the absorbance measurements are presented in TABLE 10. The net absorbance difference, 0.002 absorbance unit, for measurement of the two solutions corresponds to a Cr(VI) concentration below the detection limit of 0.01 mg/L. These data indicate that Cr(VI) contamination in the $Cr(NO_3)_3 \cdot 9H_2O$ salt represents less than 0.002 percent of the total chromium present.

The specificity of Method 7196 for Cr(VI) as dichromate and chromate was assessed by relative absorbance measurements of Cr(VI) solutions at the 0.05 mg/L and 0.5 mg/L concentration levels in the presence of 100X, 200X, 500X, and 1000X concentrations of Cr(III). Individual blank solutions were also prepared without Cr(VI) for each Cr(III) concentration and analyzed by DPC spectrophotometry. The absorbance data, corrected for DPC blanks, for the studies at the 0.05 mg/L and 0.5 mg/L concentrations of Cr(VI) are presented in

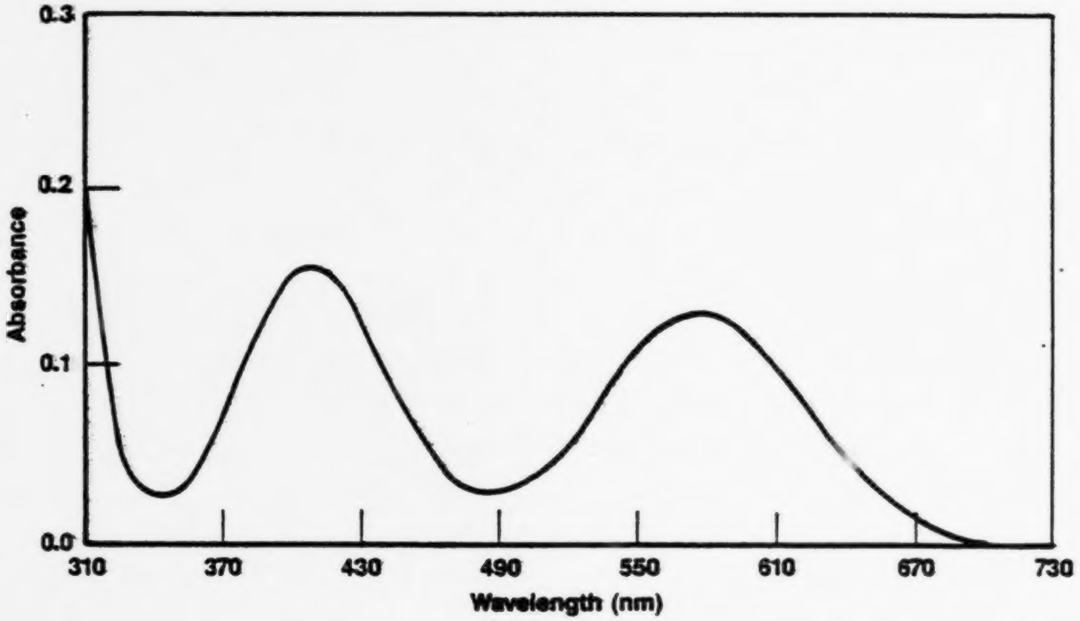

Figure 4. Absorption Spectrum for 500 mg/L Cr (III) by Diphenylcarbazide Spectrophotometry

TABLE 10. DETERMINATION OF RESIDUAL Cr(VI) IN TRIVALENT CHROMIUM NITRATE

Solution	Absorbance	Calculated Cr(VI) Concentration (mg/L)[a]
Standard Blank	0.000	--
0.05 mg/L Cr(VI)	0.043	0.049
0.50 mg/L Cr(VI)	0.440	0.500
0.75 mg/L Cr(VI)	0.661	0.749
500 mg/L Cr(III) (No DPC)	0.094	--
500 mg/L Cr(III) (+ DPC)	0.096	0.002[b]
500 mg/L Cr(III) + 0.05 mg/L Cr(VI)	0.141	0.052[c]

(a) Calculated from linear regression of 3 Cr(VI) standards.

(b) Corresponds to < 0.002 percent Cr(VI) contamination in $Cr(NO_3)_3 \cdot 9H_2O$.

(c) Recovery of 0.05 mg/L Cr(VI) spike is 100 percent.

TABLES 11 and 12, respectively. The average percent relative absorbances for 0.05 mg/L Cr(VI) as dichromate and chromate were 107 percent and 93 percent, respectively. The average percent relative absorbances for 0.5 mg/L Cr(VI) as dichromate and chromate were 99 percent and 98 percent, respectively. These data indicate excellent specificity of Method 7196 for Cr(VI) as either dichromate or chromate in the presence of 100- to 1000-fold excess concentrations of Cr(III) provided that DPC blank corrections are taken into account.

Order of Diphenylcarbazide Reagent and Sulfuric Acid Additions

Although Method 7196 specifies the addition of diphenylcarbazide reagent before acidification with sulfuric acid in the color development state, other DPC spectrophotometric methods for Cr(VI) in the literature specify acidification with sulfuric acid before addition of diphenylcarbazide reagent. The ruggedness of this procedural step for color development was examined for two concentrations of Cr(VI) in solutions of similar pH.

The results of the study for Cr(VI), as dichromate and chromate, are presented in TABLE 13. The data indicate that absorption measurements for 0.05 mg/L and 0.5 mg/L concentrations of Cr(VI), with and without 100-fold ratios of Cr(III), were not sensitive to order of additions of DPC or sulfuric acid. No differences were found for Cr(VI) added in the form of dichromate or chromate. However, addition of DPC before acidification may be preferred for analyses of alkaline sample digests to minimize the possibility of reduction of Cr(VI) by reducing species in the sample matrix prior to color development.

PHASE II - ANALYSES OF SYNTHETIC AQUEOUS SOLUTIONS

The effects of Cr(III) and sulfide matrix constituents, collectively and individually, on the DPC spectrophotometric measurements of Cr(VI) solutions were conducted. The studies focused on the examination of selected fundamental factors including concentration, pH, redox potential, and holding time of the simulated sample solution.

TABLE 11. MEASUREMENTS OF 0.05 mg/L Cr(VI) IN THE PRESENCE OF Cr(III)

Cr(III)[(a)] mg/L	Dichromate		Chromate	
	Absorbance	Percent Relative Absorbance	Absorbance	Percent Relative Absorbance[(b)]
0	0.042	--	0.045	--
5	0.042	100	0.043	96
10	0.048	114	0.041	91
25	0.044	105	0.042	93
50	0.047	112	0.042	93

(a) Cr(III) added as a solution of $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in deionized water.

(b) Relative to 0.05 mg/L Cr(VI) with no Cr(III) addition.

TABLE 12. MEASUREMENTS OF 0.5 mg/L Cr(VI) IN THE PRESENCE OF Cr(III)

Cr(III)[(a)] mg/L	Dichromate Absorbance	Dichromate Percent Relative Absorbance[(b)]	Chromate Absorbance	Chromate Percent Relative Absorbance[(b)]
0	0.415	--	0.427	--
50	0.409	99	0.419	98
100	0.411	99	0.419	98
250	0.412	99	0.418	98
500	0.412	99	0.417	98

(a) Cr(III) added as a solution of $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in deionized water.

(b) Relative to 0.5 mg/L Cr(VI) with no Cr(III) addition.

TABLE 13. EFFECT OF ORDER OF DIPHENYLCARBAZIDE REAGENT AND SULFURIC ACID ADDITIONS ON Cr(VI) ABSORBANCE MEASUREMENTS

Cr(VI) mg/L	Cr(III)[a] mg/L	Cr(VI) Absorbance			
		Dichromate		Chromate	
		DPC/H_2SO_4	H_2SO_4/DPC	DPC/H_2SO_4	H_2SO_4/DPC
0.05	0	0.042	0.042	0.043	0.043
0.05	5	0.041	0.041	0.041	0.041
0.5	0	0.412	0.409	0.409	0.419
0.5	50	0.417	0.417	0.425	0.427

(a) Cr(III) added as a solution of $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in deionized water.

pH Measurements

Selected pH measurements of Cr(VI) as dichromate and chromate at the 0.05 mg/L and 0.5 mg/L concentration levels in the presence of varying concentrations of Cr(III) and sulfide are presented in TABLE 14. The pH of each test solution was measured immediately after the addition of DPC reagent. Identical trends in solution pH were observed for Cr(VI) as either dichromate or chromate although the pH for each chromate solution was marginally higher than for the corresponding dichromate solution.

Addition of increasing Cr(III) concentrations, prepared from $Cr(NO_3)_3 \cdot 9H_2O$ as the stock source, to Cr(VI) solutions decreased the solution pH. In the presence of 500 mg/L Cr(III), the solution pH of 0.5 mg/L Cr(VI) was 2.9; such a low pH may be critical in maintaining Cr(VI) in an oxidized state if in the presence of a reducing agent that does not have alkaline properties. Addition of 5 mg/L sulfide to Cr(VI) solutions containing 5 mg/L Cr(III) increased the solution pH to where it was almost neutral. In the presence of 50 mg/L sulfide, the pH of 0.5 mg/L Cr(VI) solutions, with and without 50 mg/L Cr(III), was 4.9 and 10.6, respectively. Thus, for the given concentrations, sulfide may not reduce Cr(VI) in the absence of any acidic matrix components because of the inherent alkaline properties of sulfide.

Effect of Holding Time on Acidic Cr(VI) Solutions

Synthetic aqueous solutions containing 0.5 mg/L Cr(VI), 50 mg/L Cr(III) and 50 mg/L sulfide were prepared. Hexavalent chromium was studied by using both dichromate and chromate as stock solutions for Cr(VI). The pH of the solutions was 4.9. The buffering capacity of 50 mg/L Cr(III) prevented sulfide from raising the solution pH to approximately 11. The test solutions were analyzed for Cr(VI) by DPC spectrophotometry after holding times of 0, 12, and 60 minutes.

The results of the DPC spectrophotometric measurements of the test solutions are presented in TABLE 15. Within the 12 minute holding period, sulfide had sufficient reaction time to reduce Cr(VI) to a concentration level approximately 50 percent of its original concentration. Within the 60 minute holding time, the Cr(VI) concentration had been reduced to approximately 10 percent of its original concentration.

TABLE 14. pH MEASUREMENTS OF SIMULATED AQUEOUS SAMPLES CONTAINING Cr(VI), Cr(III) AND SULFIDE

Cr(VI) mg/L	Cr(III)[a] mg/L	Sulfide[b] mg/L	Dichromate pH	Chromate pH
0	0	0	5.8	5.9
0.05	0	0	5.6	6.0
0.05	5	0	4.0	4.2
0.05	10	0	3.9	4.0
0.05	25	0	3.6	3.8
0.05	50	0	3.4	3.6
0.05	5	5	6.9	7.0
0.5	0	0	5.9	6.6
0.5	50	0	3.5	3.6
0.5	100	0	3.3	3.4
0.5	250	0	3.1	3.2
0.5	500	0	2.9	3.0
0.5	5	5	6.7	6.7
0.5	0	50	10.6	10.6
0.5	50	50	4.9	4.9

(a) Cr(III) added as a solution of $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in deionized water.

(b) Sulfide added as a solution of Na_2S dissolved in deionized water.

TABLE 15. EFFECT OF HOLDING TIME ON ACIDIC Cr(VI) SOLUTIONS CONTAINING Cr(III) AND SULFIDE

Cr(VI) mg/L	Cr(III)(a) mg/L	Sulfide(b) mg/L	pH	Holding Time Minutes	Cr(VI) Absorbance Dichromate	Cr(VI) Absorbance Chromate
0.5	50	50	4.9	0	0.32	0.34
0.5	50	50	4.9	12	0.15	0.17
0.5	50	50	4.9	60	0.042	0.038

(a) Cr(III) added as a solution of $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in deionized water.

(b) Sulfide added as a solution of $Na_2S \cdot 9H_2O$ dissolved in deionized water.

The reduction of Cr(VI) by sulfide was exacerbated because the simulated solutions contained Cr(III); the addition of Cr(III) as trivalent chromium nitrate increased the acidity of the solution to a critical point where Cr(VI) is a more powerful oxidant and is, thus, more easily reduced by sulfide. These data verify that Cr(VI) would be reduced by sulfide in acidic media; the kinetics of the reduction may be controlled by the degree of acidity. Similar results were obtained for Cr(VI) as dichromate and chromate.

Effect of Holding Time on Alkaline Cr(VI) Solutions

The effect of sulfide on the stability of 0.5 mg/L Cr(VI) as dichromate in alkaline solution was studied as a function of holding time over a one-hour period. The pH of the Cr(VI) solutions containing 50 mg/L sulfide is 10.6 without the buffering capacity of 50 mg/L Cr(III) as the nitrate. The data, presented in TABLE 16, reveals that there is no significant reduction of 0.5 mg/L Cr(VI) in the presence of 50 mg/L sulfide over at least a 1 hour period. This confirms that Cr(VI) is stable in the presence of sulfide in an alkaline (pH 10.6) medium.

Stability of Cr(VI) Solutions

The stability of simulated aqueous solutions containing 0.05 mg/L Cr(VI) as chromate and various concentration ratios of sulfide were studied over a minimal two-day period. The pH of each solution was allowed to reach its equilibrium value without any additions to intentionally drive the pH to either the acidic or alkaline side. Measurements of solution pH and redox potentials were performed on each simulated sample at different stages in the procedure in an attempt to correlate observed decreases in Cr(VI) absorbance with possible changes in solution chemistry.

The results of the stability study are summarized in TABLE 17. No significant changes in absorbance for Cr(VI) solutions in the absence of sulfide were observed over the two-day period. A decrease (approximately 25 percent) in absorbance was observed for the Cr(VI) solutions in the presence of 10-fold sulfide concentration (0.5 mg/L) during the first 18 hours after which the absorbances remained relatively constant. No significant decreases in absorbance were observed for the Cr(VI) solutions containing 100-fold sulfide

TABLE 16. EFFECT OF HOLDING TIME ON 0.5 mg/L Cr(VI) AS DICHROMATE IN THE PRESENCE OF SULFIDE IN ALKALINE SOLUTION

Sulfide[a] mg/L	Holding Time[b] Minutes	Cr(VI) Absorbance	Relative Absorbance[c] Percent
0	0	0.411	--
50	0	0.390	95
50	10	0.379	92
50	20	0.383	93
50	30	0.386	94
50	60	0.384	93

(a) Sulfide prepared from $Na_2S \cdot 9H_2O$ dissolved in deionized water.

(b) Time elapsed between preparation of simulated aqueous sample solution and addition of diphenylcarbazide reagent and sulfuric acid in color development stage.

(c) Relative to 0.5 mg/L Cr(VI) with no sulfide addition.

TABLE 17. STABILITY OF 0.05 mg/L Cr(VI) AS CHROMATE IN AQUEOUS SULFIDE SOLUTIONS

After Cr(VI)/H_2O Addition[a]		Sulfide Addition[c]	After Sulfide Addition		Elapsed Time[d]	After Elapsed Time		After DPC Addition		Cr(VI)
pH	Redox Pot.[b]	mg/L	pH	Redox Pot.[b]	Hours	pH	Redox Pot.[b]	pH	Redox Pot.[b]	Absorbance
6.0	+160	0	--	--	0	--	--	5.8	+259	0.045
6.0	+111	0	--	--	6	5.8	+110	6.1	+178	0.043
5.8	+236	0	--	--	20	5.8	--	6.1	+261	0.040
6.1	+209	0	--	--	28	5.9	+49	5.8	+124	0.043
6.1	+204	0	--	--	47	5.8	+171	5.7	+211	0.040
5.8	+82	0.5	7.5	-231	0	--	--	6.7	+268	0.045
6.0	+105	0.5	7.2	-220	18	6.6	-186	6.7	+90	0.034
6.1	+81	0.5	7.6	-219	24	6.4	-124	6.3	+73	0.032
5.9	+99	0.5	7.2	-216	42	6.4	+78	6.3	+83	0.034
5.9	+115	0.5	7.2	-214	47	6.2	+144	6.2	+123	0.034
5.9	+119	5	9.7	-297	0	--	--	9.6	+5	0.045
5.9	+111	5	9.7	-302	6	9.1	-279	9.0	+10	0.042
5.7	+102	5	9.7	-302	21	8.7	-295	8.7	+14	0.040
5.6	+130	5	9.6	-303	24	8.8	-271	8.5	+24	0.042
5.7	+148	5	9.6	-319	90	7.7	-243	7.6	+38	0.025
5.8	+149	50	10.6	-368	0	--	--	10.6	-28	0.040
6.0	+78	50	10.8	-349	7	10.5	-330	10.4	-8	0.035
5.7	+118	50	10.7	-364	17	10.5	-337	10.0	-19	0.028
5.9	+98	50	10.7	-339	30	10.2	-316	10.1	0	0.022
5.9	+96	50	10.7	-346	48	10.3	-306	10.3	+12	0.025
5.8	+90	50	10.7	-344	93	--	--	--	+26	0.021

(a) Cr(VI) aliquot added to 100-mL volumetric flask and diluted to approximately 80 mL with deionized water of natural pH for measurements.
(b) Redox potential measurements in units of millivolts.
(c) Sulfide prepared from Na_2S dissolved in deionized water.
(d) Time elapsed between preparation and analysis of simulated sample.

concentration (5 mg/L) over the first 24-hour period; a significant decrease was observed after 90 hours. A small decrease in absorbance was observed for Cr(VI) solutions in the presence of 1000-fold sulfide concentration (50 mg/L) within the first eight hours; the absorbances were relatively constant after 24 hours for the remaining 3-day period.

A trend between the relationship of sulfide concentration with that of solution pH, redox potential and Cr(VI) absorbance was evident. For the 0.05 mg/L Cr(VI) solutions containing increasing concentrations of sulfide, the following observations were evident in TABLE 17: (1) the solution pH increased with increasing sulfide concentation, (2) the redox potential became increasingly more negative as a function of holding time with increasing sulfide concentration prior to DPC addition, or increasingly less positive after DPC addition, (3) Cr(VI) absorbances generally decreased with increasing sulfide concentration although an apparent equilibrium concentration approximately 50 percent of the original Cr(VI) concentration was reached for the higher sulfide concentrations.

The stability of simulated aqueous solutions containing 0.05 mg/L Cr(VI) as chromate and various concentration ratios of sulfide after acid preservation with nitric acid (pH adjustment to 2) was studied. The stability of Cr(VI) in these solutions were monitored for at least 24 hours.

The Cr(VI) absorbance data are presented in TABLE 18. No significant decrease in absorbance was observed for 0.05 mg/L Cr(VI) solutions in the absence of sulfide at pH 2 for up to 96 hours. However, dramatic decreases in absorbances for 0.05 mg/L Cr(VI) solutions containing as little as 0.5 mg/L sulfide at pH 2 were observed due to the reduction of Cr(VI) by sulfide under these pH conditions.

The experimental data in TABLE 18 indicate that acid preservation by acidification to pH 2 with nitric acid should not be recommended for 0.05 mg/L Cr(VI) solutions containing sulfide and other similar sample solutions. Cr(VI) solutions are not stable under these pH conditions. Moreover, this emphasizes the importance of adding DPC first before acidification with sulfuric acid, as specified in Method 7196, for DPC spectrophotometric measurements of Cr(VI) in the presence of sulfide and probably other strong reducing agents.

TABLE 18. STABILITY OF SIMULATED AQUEOUS SAMPLE SOLUTIONS(a) ACIDIFIED TO pH 2 WITH NITRIC ACID

Elapsed Time(b) Hours	Sulfide Addition(c) mg/L	Cr(VI) Absorbance
0	0	0.044
6	0	0.045
24	0	0.038
32	0	0.038
50	0	0.038
96	0	0.039
0	0.5	0.042
6	0.5	0.019
24	0.5	0.004
50	0.5	0.001
96	0.5	0.000
0	5	0.040
6	5	0.000
24	5	0.000
0	50	0.011
6	50(d)	0.000
24	50(d)	0.000

(a) Simulated sample solutions consist of 0.05 mg/L Cr(VI) as chromate and varying concentrations of sulfide.

(b) Time elapsed between preparation and analysis of simulated sample.

(c) Sulfide prepared from Na_2S dissolved in deionized water.

(d) Simulated sample became cloudy in approximately 4 hours after preparation and was filtered through a 0.22 µm disposable filter prior to colorimetric measurement.

PHASE III - ANALYSES OF INSOLUBLE STANDARD CHROMATES

Selected sample preparation procedures (e.g., alkaline, nitric acid and nitric acid/persulfate digestions) were investigated for the analyses of insoluble chromates. Preliminary experiments investigating the effects of organic filter media during filtrations of sample digest solutions and heating on the solubility characteristics of Cr(III) were first conducted.

Stability of Cr(VI) in Alkaline and Nitric Acid Digest Solutions During Vacuum-Filtration Through Organic Filter Membranes

Researchers have reported significant reduction of Cr(VI) to Cr(III) in a recent article pertaining to acid leaching of hexavalent chromium from cellulose ester filters.[10] Since both acid and alkaline digest solutions will be filtered through Millipore HA type (cellulose ester) filter membranes, it was essential to determine whether or not the filter membranes would affect the redox states of chromium.

The diameter of each filter is 47 mm and the thickness is no more than 150 um +/- 10 um. The average pore size is 0.45 µm +/- 0.02 µm. The filter is composed of mixed esters of cellulose. According to the manufacturer's literature, these filters are not attacked by dilute acids and alkalies and are recommended for temperatures under 75°C.

This study was divided into two parts: (1) filtration of acid solutions and (2) filtration of alkaline solutions. In both parts, solutions containing known concentrations of Cr(VI) were prepared in the appropriate digest medium and vacuum-filtered through cellulose ester filter membranes. The filtrate solutions were analyzed for Cr(VI) by DPC spectrophotometry. Control solutions were prepared and analyzed similarly but without the filtration step. The concentration difference measured this way would yield the net effect of the filter membrane on the stability of hexavalent chromium in the particular digestion medium.

For the vacuum-filtration of alkaline Cr(VI) solutions, duplicate solutions containing 50 µg and 500 µg of Cr(VI) as chromate were added to 50 mL of alkaline digestion medium (2 percent sodium hydroxide and 3 percent sodium carbonate). These solutions were vacuum-filtered, transferred to 100-mL volumetric flasks, and then diluted to calibrated volume with deionized water. The Cr(VI) concentrations in 10-fold dilutions of these filtrate solutions were measured by DPC spectrophotometry. Corresponding control solutions of Cr(VI), not taken through the vacuum-filtration step, were also prepared and analyzed by DPC spectrophotometry.

For the vacuum-filtration of Cr(VI) solutions in nitric acid, six solutions were used to form three sample sets: (1) duplicate solutions containing 0.2 mg Cr(VI) in 50 mL of 50 percent (v/v) nitric acid, (2) duplicate solutions containing 0.5 mg Cr(VI) in 50 mL of 10 percent (v/v) nitric acid and (3) duplicate solutions containing 0.5 mg Cr(VI) in 50 mL of 50 percent (v/v) nitric acid. These solutions were filtered, transferred and diluted to 100 mL in volumetric flasks and further diluted 10-fold for DPC spectrophotometry. No pH adjustment for color development was required for these sample solutions. Corresponding control solutions were prepared by adding either 2-mL or 5-mL aliquots of 10 mg/L Cr(VI) standard to 5 mL of the appropriate acid medium and diluted to 100 mL for DPC analysis. The pH of these acid solutions was less than 1. Another set of control solutions were pH adjusted to pH 2 so the pH factor would not be compounded with the filter membrane factor.

The calibration curves for this study were constructed with Cr(VI) standards prepared in deionized water. Deionized water was used as the reference. The results for this filter membrane study are summarized in TABLE 19. There was no significant loss of Cr(VI) when alkaline solutions or 10 percent (v/v) nitric acid solutions were filtered through the cellulose ester membranes. However, when the medium is 50 percent (v/v) nitric acid, significant loss of Cr(VI) through reduction to Cr(III) was found. This conclusion is supported by combined DPC spectrophotometric and ICP-OES results.

The extent of Cr(VI) reduction is approximately 90 μg regardless of whether 0.2 mg or 0.5 mg of Cr(VI) were available. This constant amount of Cr(VI) reduction could be a function of surface area contact and/or duration of contact with the filter membrane. It is uncertain whether the cellulose esters are being oxidized by the Cr(VI) and as a result, a portion of the Cr(VI) is reduced or whether the filters are contaminated with trace amounts of metals such as Fe(II).

TABLE 19. EFFECT OF ORGANIC FILTER MEMBRANE ON THE STABILITY OF HEXAVALENT CHROMIUM IN ACID AND ALKALINE MEDIA

Test Solutions	Percent Recovery of Cr(VI) DPC (1)	Percent Recovery of Cr(VI) DPC (2)	Percent Recovery of Cr(VI) ICP (1)	Percent Recovery of Cr(VI) ICP (2)
Alkali Digestion Medium				
0.05 mg Cr(VI)	96	98	--	--
0.05 mg Cr(VI) Control	96	--	--	--
0.5 mg Cr(VI)	99	98	--	--
0.5 mg Cr(VI) Control	100	--	--	--
Acid Digestion Medium				
0.5 mg Cr(VI)/10% (v/v) HNO_3, pH = 1.2	96	96	--	--
0.5 mg Cr(VI)/10% (v/v) HNO_3 Control, pH = 1.2	99	--	--	--
0.5 mg Cr(VI)/10% (v/v) HNO_3 Control, pH = 2	102	--	--	--
0.2 mg Cr(VI)/50% (v/v) HNO_3 pH = 0.6	47	47	99	98
0.2 mg Cr(VI)/50% (v/v) HNO_3 Control, pH = 0.6	92	--	--	--
0.2 mg Cr(VI)/50% (v/v) HNO_3 Control, pH = 2	99	--	--	--
Net reduction = 89 ug Cr(VI) to Cr(III)				
0.5 mg Cr(VI)/50% (v/v) HNO_3, pH = 0.6	71	73	97	100
0.5 mg Cr(VI)/50% (v/v) HNO_3 Control, pH = 0.6	90	--	--	--
0.5 mg Cr(VI)/50% (v/v) HNO_3 Control, pH = 2	102	--	--	--
Net reduction = 91 ug Cr(VI) to Cr(III)				

Effect of Heating on the Solubility Characteristics of Cr(III) in Alkaline Digestion Medium

Chromium (III) is only sparingly soluble in alkaline medium since the solubility product constant, K_{sp}, of $Cr(OH)_3$ is approximately 10^{-31}. In the presence of excess hydroxide, $Cr(OH)_3$ can be resolubilized through the formation of $Cr(OH)_4^-$ species. The formation constant, K_f, of $Cr(OH)_4^-$ from $Cr(OH)_3$ and OH^- ions is $10^{-0.4}$.

To provide an estimate of chromium (III) precipitation without sample matrix interference, duplicate solutions were prepared by adding 50 mL of alkaline digestion medium to 7.8 mg Cr(III). One solution was heated for 45 minutes at 80°C +/- 10°C with mechanical stirring. The other solution was maintained at room temperature for 24 hours. When the alkaline digestion medium was added to each Cr(III) mass, a light-blue precipitate formed which quickly redissolved to form a light-green solution as more alkaline solution was added. The heated solution formed a fine light-blue precipitate whereas the unheated solution remained light green. No precipitate was observed in the unheated solution. Both solutions were filtered. The light-blue precipitate in the heated solution was retained on a 0.45-µm pore size filter membrane; the filtrate was clear.

Analyses of the filtrates by ICP-OES revealed that 7.0 mg/L chromium remained in solution for the unheated solution, which represents 90 percent of the original 7.8 mg/L chromium concentration. The filtrate from the heated solution contained only 0.13 mg/L dissolved chromium, representing only 2 percent of the original 7.8 mg/L chromium concentration. These data provide qualitative confirmation that aqueous trivalent chromium is largely removed from the dissolved fraction through precipitation as a hydroxide after digestion in alkaline media.

Effects of Nitric Acid and pH on Diphenylcarbazide

The digestion methods using a nitric acid medium result in highly acidic digests (generally less than pH 1) that may need to be analyzed for Cr(VI) by the DPC spectrophotometric method. Because of the highly acidic and oxidizing nature of the nitric acid and of the reducing characteristics of the DPC reagent, the combination of the two solutions may result in a strong interaction between the HNO_3 and DPC that may adversely effect the redox reaction between Cr(VI) and DPC in the formation of the colored complex.

Synthetic aqueous test solutions of 0.5 ppm Cr(VI) were prepared in various concentrations of HNO_3 as indicated in TABLE 20. Each test solution was prepared in duplicate for spectrophotometric measurement, one without pH adjustment and one with pH adjustment to pH 2 using dilute NaOH prior to addition of the DPC reagent.

The absorbance measurements for the paired test solutions under different pH conditions are presented in Table 20. These absorbance data indicate that at least up to 30 percent HNO_3 solutions do not significantly degrade the efficacy of the DPC reagent. Test solutions resulting from nitric acid digestions may, therefore, be analyzed directly by the DPC spectrophotometric method without previously raising the pH of the test solution to pH 2.

Alkaline Digestions of Insoluble Chromates in the Presence of Cr(III)

The alkaline digested method was investigated to ascertain whether or not it could solubilize chromates typically insoluble in aqueous solution and if it would oxidize Cr(III). Dichromate and insoluble chromates, spiked with two different masses of solid $Cr(NO_3)_3 \cdot 9H_2O$, were analyzed by DPC spectrophotometry following alkaline digestions. In these experiments, an abbreviated method was used in which the leachate was not filtered but instead diluted to calibrated volume without pH adjustment. Lead chromate in the test sample did not visibly precipitate because a small mass was used and the alkaline leachate solution was diluted considerably before an aliquot was neutralized with nitric acid prior to the DPC spectrophotometric measurement.

As indicated by the measured absorbances in TABLE 21, good recoveries of Cr(VI) were obtained and Cr(III) was not significantly oxidized during the alkaline digestion in the absence of other oxidizing compounds. For the present test conditions, the alkaline digestion method proved satisfactory in terms of solubilizing Cr(VI) from insoluble chromates and not oxidizing Cr(III) in alkaline media.

TABLE 20. RESULTS OF DIPHENYLCARBAZIDE SPECTROPHOTOMETRIC MEASUREMENTS OF 0.5 mg/L Cr(VI) SOLUTIONS IN VARYING CONCENTRATIONS OF NITRIC ACID

Percent HNO_3 Matrix	Absorbance	
	Without pH Adjustment	With pH Adjustment(a)
0	0.428(b)	0.420
1	0.422	0.422
5	0.402	0.420
10	0.420	0.420
20	0.410	0.418
30	0.400	0.408

(a) Solution pH adjusted to pH 2 with dropwise additions of one molar or ten molar NaOH.

(b) Test solution without HNO_3 required 0.2 mL of 10 percent H_2SO_4 for adjustment of solution pH to pH 2 for color development.

TABLE 21. RESULTS OF ANALYSES OF DICHROMATE AND INSOLUBLE CHROMATES IN THE PRESENCE OF TRIVALENT CHROMIUM FOLLOWING ALKALINE DIGESTIONS

Sample[a,b,c]	Absorbance
Blank	
+ 0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ (100 mg Cr)	0.004
+ 7.7 g $Cr(NO_3)_3 \cdot 9H_2O$ (1000 mg Cr)	0.004
155 mg $PbCrO_4$ (25 mg Cr)	
+ 0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ (100 mg Cr)	0.410
+ 7.7 g $Cr(NO_3)_3 \cdot 9H_2O$ (1000 mg Cr)	0.414
122 mg $BaCrO_4$ (25 mg Cr)	
+ 0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ (100 mg Cr)	0.414
+ 7.7 g $Cr(NO_3)_3 \cdot 9H_2O$ (1000 mg Cr)	0.414
70.8 mg $K_2Cr_2O_7$ (25 mg Cr)	
+ 0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ (100 mg Cr)	0.396
+ 7.7 g $Cr(NO_3)_3 \cdot 9H_2O$ (1000 mg Cr)	0.396
70.8 mg $K_2Cr_2O_7$ (25 mg Cr) (aqueous standard solution)	0.402

(a) All Cr(VI) salts added so that Cr(VI) concentration would be 0.5 mg/L in final dilution for analysis.

(b) Sample leachate solutions not filtered; initially diluted to 1000 mL volume without pH adjustment.

(c) 2-mL aliquots of leachate solutions diluted to about 30 mL volume with deionized water; pH adjusted to approximately 7 with NaOH prior to DPC/H_2SO_4 addition and final dilution to 100 mL volume for colorimetric measurement.

Alkaline Digestions of Barium Chromate

Alkaline digestions were evaluated to ascertain the extent of any reduction of Cr(VI) during the digestions of an insoluble chromate. Barium chromate, selected as the insoluble chromate for testing, was studied in the absence and presence of two different reducing compounds, sodium sulfide and ascorbic acid, each at two different concentrations.

Test portions (487 mg) of solid barium chromate (equivalent to 100 mg of hexavalent chromium) containing additions of sodium sulfide or ascorbic acid were digested according to the alkaline digestion procedure; sulfide and ascorbic acid were added individually in two different amounts equivalent to a one- and ten-fold ratio of the Cr(VI) mass in the barium chromate. The alkaline digestions and analyses for each of the test samples were repeated on separate days to confirm the experimental observations and data.

Observations and results of the analyses of barium chromate solutions for alkaline digestions are presented in TABLE 22. A fine precipitate formed during the alkaline digestions of all barium chromate test samples. The precipitates observed for all the barium chromate test samples except the one with high-level sulfide were white; a yellowish-green precipitate was observed for barium chromate with high-level sulfide. The white precipitates were probably barium carbonate; chromium (III) hydroxide may have also coprecipiated. The yellow-green precipitate was probably a mixture of barium carbonate and elemental sulfur which was visible only for the higher sulfide mass addition.

Serial dilutions of 10-fold and 20-fold for a combined 200-fold dilution were performed on the filtrate of each barium chromate test sample to provide a target concentration of 0.5 ppm Cr(VI) for spectrophotometric analyses. In the absence of reducing compounds, an average absorbance of 0.413 (approximately 97 percent of an aqueous 0.5 ppm Cr(VI) calibration standard) was measured for the test solutions which represents full recovery of Cr(VI). Average recoveries of approximately 85 percent and 89 percent were obtained for Cr(VI) in the barium chromate test samples containing equivalent amounts of sulfide or ascorbic acid, respectively. No detectable Cr(VI) was measured in the barium chromate samples containing sulfide or ascorbic acid at 10-fold greater masses.

TABLE 22. RESULTS OF ANALYSES OF BARIUM CHROMATE SOLUTIONS FOLLOWING ALKALINE DIGESTIONS

Sample	Sample Digest Appearance		Percent Reduction of Cr(VI)	
	Precipitate	Filtrate	#1	#2
487 mg $BaCrO_4$ (100 mg Cr)	white	yellow	4	2
+ 0.243 g Na_2S (0.1 g sulfide)	white	yellow[a]	15	16
+ 2.43 g Na_2S (1 g sulfide)	yellow-green	colorless[a]	100	100
+ 0.1 g Ascorbic Acid	white	golden brown	8	14
+ 1 g Ascorbic Acid	white	brown	100	100

(a) Alkaline sample filtrate solutions turned cloudy upon neutralization with nitric acid.

The data in TABLE 22 indicate: (1) Cr(VI) is completely solubilized and is not significantly reduced during the alkaline digestions of insoluble barium chromate in the absence of representative reducing compounds, (2) approximately 10 to 15 percent of the Cr(VI) is reduced to Cr(III) during the alkaline digestions of insoluble barium chromate in the presence of sulfide or ascorbic acid at equivalent mass ratios of reducing species to Cr(VI) in the barium chromate, and (3) Cr(VI) is completely reduced to Cr(III) during the alkaline digestions of insoluble barium chromate in the presence of sulfide or ascorbic acid at mass ratios 10-fold greater than Cr(VI) in the barium chromate. Reduction of Cr(VI) occurred, even under alkaline conditions, although the extent of such redox behavior may be more significant under solution conditions of low pH.

The complete reduction of Cr(VI) in the presence of 10-fold ratios of sulfide during alkaline digestions (pH approximately 12) conflicts with previous data (TABLE 16) in which Cr(VI) in simulated solutions containing 100-fold ratios of sulfide (pH 10.6) was not significantly reduced. The data suggest that reduction of Cr(VI) in alkaline media may be promoted through heating and mixing effects.

Nitric Acid Digestions of Barium Chromate

The solubilization of Cr(VI) from an insoluble chromate and redox behavior in acid media were examined. Test portions (487 mg) of barium chromate containing different additions of sodium sulfide or ascorbic acid were digested using a nitric acid digestion method. The test samples are the same types as those studied for the preceding alkaline digestions. Serial dilutions of 10-fold and 20-fold for a combined 200-fold dilution were performed on the filtrate of each barium chromate test solution to provide a target concentration of 0.5 mg/L Cr(VI) for spectrophotometric analyses. The nitric acid digestions and analyses for each of the test samples were repeated on separate days to confirm the experimental observations and data.

Observations and results of the analyses of barium chromate test solutions for nitric acid digestions are presented in TABLE 23. Whereas a fine precipitate formed during the alkaline digestions of each of the barium chromate test samples, no visible precipitates were observed for any of the same test samples during the nitric acid digestions. Of all the sample test

TABLE 23. RESULTS OF ANALYSES OF BARIUM CHROMATE SOLUTIONS FOLLOWING NITRIC ACID DIGESTIONS

Sample	Sample Digest Appearance		Percent Reduction of Cr(VI)	
	Precipitate	Filtrate	#1	#2
487 mg $BaCrO_4$ (100 mg Cr)	none	yellow	3	6
+ 0.243 g Na_2S (0.1 g sulfide)	none	yellow-green	94	100
+ 2.43 g Na_2S (1 g sulfide)	none	blue(a)	100	100
+ 0.1 g Ascorbic Acid	none	blue-light red	100	100
+ 1 g Ascorbic Acid	none	blue-red	100	100

(a) Sample digest solution had cloudy appearance before filtering.

solutions, only the barium chromate with high-level sulfide formed a cloudy solution before filtering, presumably due to tiny particles of elemental sulfur.

In the absence of reducing compounds, an average absorbance of 0.408 (approximately 96 percent of an aqueous 0.5 mg/L Cr(VI) calibration standard) was measured for the test solutions representing full recovery of Cr(VI). However, Cr(VI) was completely reduced in all the barium chromate test samples containing reducing compounds. These experimental data confirm that Cr(VI) is more easily reduced to Cr(III) under strongly acidic conditions.

Alkaline Digestions of Trivalent Chromium Nitrate

Test portions (0.77 g and 7.7 g) of solid trivalent chromium nitrate (equivalent to 0.1 g and 1 g of trivalent chromium, respectively) were digested according to the alkaline digestion procedure to ascertain the extent of any oxidation of Cr(III) in alkaline media. Persulfate and manganese dioxide were also added individually in two different amounts equivalent to one- and 10-fold ratios of the Cr(III) mass in the chromium nitrate. The alkaline digestions and analyses for each of the test samples were repeated on separate days to confirm the experimental observations and data.

Fluffy white precipitates were observed in the initial alkaline digestions of trivalent chromium nitrate with and without potassium persulfate additions. The relative amounts of the precipitates were inversely proportional to the amounts of $K_2S_2O_8$ added; the largest amount of precipitate was observed with no addition of $K_2S_2O_8$ and the smallest amount of precipitate was observed with the largest $K_2S_2O_8$ addition. Whereas Cr(III) is sparingly soluble in alkaline media, the presence of persulfate may oxidize Cr(III) during the digestions to Cr(VI) which is soluble in alkaline media.

The relative extents of oxidation of Cr(III) to Cr(VI) during the alkaline digestions were ascertained by analyzing appropriate dilutions of the sample digests for Cr(VI) by DPC spectrophotometry. The results of the analyses of trivalent chromium nitrate solutions for alkaline digestions are presented in TABLE 24. Based on the DPC spectrophotometric measurements for Cr(VI), less than 0.1 percent oxidation of Cr(III) was observed for both concentrations of trivalent chromium nitrate in the absence of oxidizing compounds. Approximately 17 percent and 80 percent oxidations of Cr(III) were

TABLE 24. RESULTS OF ANALYSES OF TRIVALENT CHROMIUM NITRATE SOLUTIONS FOLLOWING ALKALINE DIGESTIONS

	Sample Digest Appearance		Percent Oxidation of Cr(III)	
Sample	Precipitate	Solution	#1	#2
0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ (0.1 g Cr)	blue	colorless	<0.1[a]	<0.1
+ 0.141 g $K_2S_2O_8$ (0.1 g persulfate)	yellow-green	faint yellow	17[a]	18
+ 1.41 g $K_2S_2O_8$ (1 g persulfate)	yellow-green	yellow	71[a]	71
+ 0.1 g MnO_2	blue-green	colorless	0.6	0.4
+ 1 g MnO_2	blue-green	faint yellow	3	6
7.7 g $Cr(NO_3)_3 \cdot 9H_2O$ (1 g Cr)	blue-green	colorless	<0.1[b]	<0.1
+ 1.41 g $K_2S_2O_8$(1 g persulfate)	yellow-green	faint yellow	17[b]	16
+ 14.1 g $K_2S_2O_8$ (10 g persulfate)	yellow-green	yellow	88[b]	86
+ 1 g MnO_2	blue-green	faint yellow	0.1	0.2
+ 10 g MnO_2	blue-green	yellow	0.7	1

(a) Sample digests filtered through 0.45-μm filter by vacuum filtration prior to dilution to one liter calibrated volume; all remaining test solutions diluted to one liter calibrated volume without vacuum filtration allowing fluffy precipitate to settle to bottom.

(b) Test samples analyzed for Cr(VI) by DPC colorimetric method after digested samples diluted to one liter calibrated volume and stored over the weekend; all remaining test solutions analyzed later in same day of sample digestions.

observed for the alkaline digestions of trivalent chromium nitrate in the presence of persulfate at 1- and 10-fold mass ratios of the Cr(III) mass in the original test material, respectively. Approximately 0.3 percent and 3 percent oxidations of Cr(III) were observed for the alkaline digestions of trivalent chromium nitrate in the presence of manganese dioxide at 1- and 10-fold mass ratios of the Cr(III) mass in the original test material, respectively.

Based on the observed oxidations of Cr(III), although to different extents, in a standard trivalent chromium sample in the presence of two different oxidizing compounds, the alkaline digestion method may be unsatisfactory for the digestions of solid environmental samples of unknown composition and redox properties in which Cr(VI) must be determined. Significant oxidation of endogenous Cr(III) during the alkaline digestion of an environmental sample would result in a positive bias in the Cr(VI) measurement.

Nitric Acid Digestions of Chromium Nitrate

Solid test portions of chromium nitrate were digested in 50 percent nitric acid media to ascertain the extent of any oxidation of Cr(III) during nitric acid digestions. Observations and results of these experiments, performed using two different masses of chromium nitrate, are presented in TABLE 25. The chromium nitrate test compounds were completely solubilized in the 50 percent nitric acid digestion medium. The blue color of the test sample digest solutions provided a qualitative measure that Cr(III) was predominately present in the solution and that little oxidation of Cr(III) to Cr(VI) had occurred. The DPC spectrophotometric measurements for Cr(VI) in the test solutions revealed that less than 0.1 percent oxidation of Cr(III) to Cr(IV) had occurred during the 50 percent nitric acid digestions.

Based on the analyses of standard test compounds, the data from TABLES 23 and 25 revealed that Cr(VI) was not significantly reduced and that Cr(III) not significantly oxidized in the 50 percent nitric acid digestion medium. Therefore, the 50 percent nitric acid medium represents a digestion method of potential feasibility for the analyses of environmental samples containing an insoluble chromate and Cr(III).

TABLE 25. RESULTS OF ANALYSES OF CHROMIUM (III) NITRATE SOLUTIONS FOLLOWING NITRIC ACID DIGESTIONS

Sample	Sample Digest Appearance		Percent Oxidation of Cr(III)	
	Precipitate	Filtrate	#1	#2
0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ (0.1 g Cr)	none	blue	<0.1	<0.1
7.7 g $Cr(NO_3)_3 \cdot 9H_2O$ (1.0 g Cr)	none	blue	<0.1	<0.1

Nitric Acid/Persulfate Digestions of Barium Chromate

The nitric acid/persulfate digestion procedure was evaluated to ascertain the extent of any reduction of Cr(VI) during the digestions of solid test portions of insoluble hexavalent chromium in the form of barium chromate. The experiments were predicated on the possibility of maintaining a highly oxidizing medium with potassium persulfate in the digestion solution to keep Cr(VI) in an oxidized state even under extremely acidic conditions. Sodium sulfide and ascorbic acid also were individually added at two different masses to the barium chromate to form reducing environments of varying strengths. The digestion medium consisted of a 50 (v/v) percent nitric acid mixture containing 5 percent (w/v) potassium persulfate.

Observations and results of the analyses of barium chromate test samples for nitric acid/persulfate digestions are presented in TABLE 26. The digestion of each test sample resulted in the formation of a precipitate, presumably due to barium sulfate. The colors of the solutions of most of the test sample digests were blue, suggesting the presence of Cr(III) from the reduction of Cr(VI). The DPC spectrophotometric measurements of the test solutions did not reveal any detectable Cr(VI), thus indicating complete reduction of Cr(VI) to Cr(III). It was not understood why Cr(VI) in the barium chromate test samples not containing reducing compounds was completely reduced to Cr(III) even under highly acidic conditions in view of the apparent oxidizing strength of potassium persulfate.

Nitric Acid/Persulfate Digestions of Chromium Nitrate

The nitric acid/persulfate digestion procedure was evaluated to ascertain the extent of any oxidation of Cr(III) during the digestions of solid test portions of chromium nitrate in the absence and presence of an additional strong oxidizing compound. The solid test samples consisted of two different masses of chromium nitrate in the absence and presence of potassium permanganate at 1- and 10-fold ratios to Cr(III).

Observations and results of the analyses of the chromium nitrate test samples for nitric acid/persulfate digestions are presented in TABLE 27. The digestion of each solid test sample resulted in the formation of a small amount of precipitate which required filtering. The colors of the test sample digest

TABLE 26. RESULTS OF ANALYSES OF BARIUM CHROMATE SOLUTIONS FOLLOWING NITRIC ACID/PERSULFATE DIGESTIONS

Sample	Sample Digest Appearance		Percent Reduction of Cr(VI)	
	Precipitate	Solution	#1	#2
487 mg $BaCrO_4$ (100 mg Cr)	white	blue	100	100
+ 0.243 g Na_2S(0.1 g sulfide)	blue-white	blue	100	100
+ 2.43 g Na_2S(1 g sulfide)	yellow-green	blue	100	100
+ 0.1 g Ascorbic Acid	yellow-blue	blue	100	100
+ 1 g Ascorbic Acid	yellow-blue	grey-black	100	100

TABLE 27. RESULTS OF ANALYSES OF CHROMIUM(III) NITRATE SOLUTIONS FOLLOWING NITRIC ACID/PERSULFATE DIGESTIONS

Sample	Sample Digest Appearance		Percent Oxidation of Cr(III)	
	Precipitate	Solution	#1	#2
0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ (0.1 g Cr)	grey-white	blue	0	0
+ 0.1 g $KMnO_4$	grey-white	blue	0	0
+ 1 g $KMnO_4$	dark-brown	golden brown	90	92
7.7 g $Cr(NO_3)_3 \cdot 9H_2O$ (1 g Cr)	yellow-green	dark blue	2	1
+ 1 g $KMnO_4$	yellow-green	yellow-brown	26	27
+ 10 g $KMnO_4$	dark brown	yellow-orange	84	84

TABLE 27. RESULTS OF ANALYSES OF CHROMIUM(III) NITRATE SOLUTIONS FOLLOWING NITRIC ACID/PERSULFATE DIGESTIONS

Sample	Sample Digest Appearance: Precipitate	Sample Digest Appearance: Solution	Percent Oxidation of Cr(III): #1	Percent Oxidation of Cr(III): #2
0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ (0.1 g Cr)	grey-white	blue	0	0
+ 0.1 g $KMnO_4$	grey-white	blue	0	0
+ 1 g $KMnO_4$	dark-brown	golden brown	90	92
7.7 g $Cr(NO_3)_3 \cdot 9H_2O$ (1 g Cr)	yellow-green	dark blue	2	1
+ 1 g $KMnO_4$	yellow-green	yellow-brown	26	27
+ 10 g $KMnO_4$	dark brown	yellow-orange	84	84

solutions before filtering ranged from blue to yellow; these colors provided qualitative indications of the extent of oxidation of Cr(III) to Cr(VI) during the digestion procedures. The DPC spectrophotometric measurements for Cr(VI) in the test solutions revealed that less than 2 percent oxidation of Cr(III) to Cr(VI) occurred for those test compounds not containing permanganate. However, oxidation of Cr(III) occurred for those test samples containing potassium permanganate; the extent of oxidation of Cr(III) was dependent on the permanganate concentration.

Effects of Nitric Acid Concentrations on Nitric Acid/Persulfate Digestions of Mixed Valence Solutions of Chromium

The results of nitric acid/persulfate digestions in TABLES 26 and 27 revealed complete reduction of Cr(VI) and no significant oxidation of Cr(III), respectively in the absence of other competing redox components. Experiments were performed to ascertain if a nitric acid concentration exists for the nitric acid/persulfate digestion medium such that Cr(VI) is not reduced or that Cr(III) is not oxidized..

Absolute masses of chromium nitrate and potassium dichromate were used to provide equivalent amounts of Cr(III) and Cr(VI) in the original solid test sample. The mass of potassium persulfate and the volume of nitric acid added to the test chromium mixture were adjusted to simulate the digestion conditions used in the previous experiments; 10-g portions of potassium persulfate in 200 mL of diluted HNO_3 provided a 5 percent (w/v) $K_2S_2O_8$ concentration in the digestion medium. The nitric acid concentrations in the digestion medium were varied between 50 percent and 0.5 percent.

Observations and results of the analyses of the Cr(III)-Cr(VI) solutions for the nitric acid/persulfate media are presented in TABLE 28. A small amount of precipitate occurred only for the digestion medium containing 0.5 percent nitric acid. The colors of the test sample digest solutions varied from blue to yellow; the color of each solution provided a qualitative indication of the dominating redox reaction occurring under the given digestion conditions. The DPC spectrophotometric measurements revealed that Cr(VI) was completely reduced to Cr(III) in 50 percent nitric acid. For the remaining test sample solutions of decreasing nitric acid concentration, oxidation of

TABLE 28. RESULTS OF ANALYSES OF CHROMIUM(III) NITRATE/POTASSIUM DICHROMATE SOLUTIONS FOLLOWING NITRIC ACID/PERSULFATE DIGESTIONS EMPLOYING VARIOUS NITRIC ACID CONCENTRATIONS

Sample	Sample Digest Appearance		Percent Oxidation of Cr(III)		Percent Reduction of Cr(VI)	
	Precipitate	Solution	#1	#2	#1	#2
0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ + 0.283 g $K_2Cr_2O_7$ + 10 g $K_2S_2O_8$ + 50 percent HNO_3	none	blue	--	--	100	100
0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ + 0.283 g $K_2Cr_2O_7$ + 10 g $K_2S_2O_8$ + 20 percent HNO_3	none	golden brown	6	2	--	--
0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ + 0.283 g $K_2Cr_2O_7$ + 10 g $K_2S_2O_8$ + 5 percent HNO_3	none	golden brown	60	81	--	--
0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ + 0.283 g $K_2Cr_2O_7$ + 10 g $K_2S_2O_8$ + 2 percent HNO_3	none	yellow	78	81	--	--
0.77 g $Cr(NO_3)_3 \cdot 9H_2O$ + 0.283 g $K_2Cr_2O_7$ + 10 g $K_2S_2O_8$ + 0.5 percent HNO_3	brown	yellow	80	83	--	--

Cr(III) to Cr(VI) was predominate. The extent of Cr(III) oxidation increased with decreasing nitric acid concentration.

The redox activity of the Cr(III)-Cr(VI) couple was extremely sensitive to nitric acid concentrations for concentrations between 50 percent and 5 percent. Below nitric acid concentrations of 5 percent, the rate of increase of Cr(III) oxidation was less dramatic. An apparent plateau region of approximately 80 percent oxidation was reached for nitric acid concentrations between 5 percent and 0.5 percent.

Between 50 percent and 20 percent nitric acid concentrations, the reduction of Cr(VI) no longer occurs and oxidation of Cr(III) begins to predominate. A nitric acid concentration between 20 percent and 50 percent may exist for the Cr(III)-Cr(VI) redox couple such that no oxidation of Cr(III) or reduction of Cr(VI) by components of the digestion medium occurs. Therefore, these data indicate that potassium persulfate has strong reducing properties in 50 percent (v/v) nitric acid media which explains the anomalous redox phenomena for Cr(VI) and Cr(III) in TABLES 26 and 27.

Nitric Acid/Persulfate Digestions of Potassium Dichromate and Chromium Nitrate at Room Temperature

An experiment was also conducted to ascertain whether the observed reduction of Cr(VI) or oxidation of Cr(III) during nitric acid/persulfate digestions is a result of heating or whether the redox reactions will occur at room temperature. Simulated nitric acid/persulfate digestions of Cr(VI), as potassium dichromate, and Cr(III), as chromium nitrate, were prepared to provide individual Cr(VI) and Cr(III) concentrations of 500 mg/L in 200 mL of 50 percent HNO_3/5 percent $K_2S_2O_8$ digestion medium. The temperature varied over a maximum 2-hour digestion period between 24°C and 31°C; the small increase in temperature over ambient temperature resulted from slight heating of the sample digests due to mechanical stirring effects during the digestion periods. The DPC spectrophotometric measurements were performed on test sample digests at 20-minute intervals for the 2-hour digestion period to provide insight into the kinetic behavior of the Cr(III)-Cr(VI) redox couple at room temperature.

The results for Cr(VI) and Cr(III) are presented in TABLES 29 and 30, respectively. The results of the first day's experiments for digestions of potassium dichromate revealed that only slight reduction of Cr(VI) occurred at room temperature; the extent of Cr(VI) reduction ranged between 2 and 6 percent

TABLE 29. RESULTS OF ANALYSES OF ROOM-TEMPERATURE[a] DIGESTIONS OF POTASSIUM DICHROMATE IN NITRIC ACID/PERSULFATE MEDIA[b]

Time from Start of Digestion, min	Percent Reduction of Cr(VI)		
	#1	#2	#3
20	3	27	32
40	4	38	50
60	4	49	62
80	6	57	71
100	2	67	79
120	4	75	85

(a) For all sets of data, temperature varied between 24-31°C.

(b) Test sample solution consists of 0.283 g $K_2Cr_2O_7$, 10 g $K_2S_2O_8$, and 200 mL 50 percent HNO_3.

TABLE 29. RESULTS OF ANALYSES OF ROOM-TEMPERATURE[a] DIGESTIONS OF POTASSIUM DICHROMATE IN NITRIC ACID/PERSULFATE MEDIA[b]

Time from Start of Digestion, min	Percent Reduction of Cr(VI)		
	#1	#2	#3
20	3	27	32
40	4	38	50
60	4	49	62
80	6	57	71
100	2	67	79
120	4	75	85

(a) For all sets of data, temperature varied between 24-31°C.

(b) Test sample solution consists of 0.283 g $K_2Cr_2O_7$, 10 g $K_2S_2O_8$, and 200 mL 50 percent HNO_3.

TABLE 30. RESULTS OF ANALYSES OF ROOM-TEMPERATURE[a] DIGESTIONS OF CHROMIUM (III) NITRATE IN NITRIC ACID/PERSULFATE MEDIA[b]

Time from Start of Digestion, min	Percent Oxidation of Cr(III)		
	#1	#2	#3
20	0	0	0
40	0	0	0
60	0	0	0
80	0	0	0
100	0	0	0
120	0.6	0	0

(a) For all sets of data, temperature varied between 24-31°C.

(b) Test sample solution consists of 0.77 g $Cr(NO_3)_3 \cdot 9H_2O$, 10 g $K_2S_2O_8$, and 200 mL 50 percent HNO_3.

over the 2-hour digestion period with no trend of time dependency. However, the results of the experiments repeated on a second day differed significantly from those of the previous day. For the second day's experiments, 27 percent reduction of Cr(VI) occurred during the first 20 minutes of digestion. The extent of Cr(VI) reduction continued to increase with prolonged digestion time; 75 percent reduction of Cr(VI) had occurred at the end of the 2-hour digestion period. Due to the discrepancy between the results of the same experiments performed on separate days, the experiments were repeated for a third time.

The analytical data in TABLE 29 indicate that the results of the third day's experiments confirmed the results of the second day's experiments. The combined results indicate that approximately 30 percent reduction of Cr(VI) occurred during the first 20 minutes of the digestion and continued to increase with digestion time; approximately 80 percent reduction of Cr(VI) had occurred by the end of the 2-hour digestion period.

A summary of the results in TABLE 29 reveals that Cr(VI) is reduced at room temperature under these digestion conditions. Therefore, the digestion medium consisting of 50 percent nitric acid and 5 percent potassium persulfate is not suitable for room-temperature digestions of solid materials.

Room-temperature digestions using the nitric acid/persulfate medium were evaluated for chromium nitrate; the results are presented in TABLE 30. The results of three sets of experiments, conducted on separate days, reveal that Cr(III) oxidation does not occur over the entire 2-hour digestion period at room temperature using this digestion medium.

Aqueous Potassium Persulfate Digestions

The feasibility of digestions of an insoluble chromate test compound (barium chromate) using a 5 percent (w/v) potassium persulfate solution in deionized water without nitric acid was investigated. The evaluation of this digestion medium was based on two criteria: (1) the extent to which barium chromate test samples were solubilized, and (2) the extent to which Cr(III) test samples were oxidized.

Duplicate 487-mg test portions of barium chromate, equivalent to 100 mg of Cr(VI), were weighed and transferred to individual 500-mL beakers. Duplicate 770-mg test portions of $Cr(NO_3)_3 \cdot 9H_2O$, equivalent to 100 mg of Cr(III), were weighed and transferred into individual 500-mL beakers.

Duplicate method blanks were also carried through the entire analytical procedure. Each test sample was digested in 200-mL of persulfate medium (pH of approximately 4.0) on a hot plate with mechanical stirring for two hours. The sample solutions were heated to a temperature of approximately 80°C. After cooling in a water bath, the sample digest solutions were vacuum-filtered, with deionized water rinsing, through a 47-mm filter (0.45-μm pore size) of a glass Millipore filtering apparatus, and transferred into 1-L volumetric flasks. The sample filtrate solutions were then diluted to calibrated volume with deionized water, providing target chromium concentrations equivalent to 100 mg/L in solution.

Upon initiation of the digestion procedure, the barium chromate test solutions turned yellow in color with a cloudy appearance; the Cr(III) test solutions turned from an initial blue color to an intermediate green color and then a bright-yellow color during the first 30 minutes of the digestions. Upon filtration of the barium chromate digest solutions, the filtrate solutions were bright yellow-orange in color; solid material of light-yellow color was retained on the filter membranes. The filtrate solutions of the Cr(III) samples were bright yellow in color; no visible solid material was retained on the filter membranes.

Each of the 1-L filtrate solutions was diluted 10-fold with deionized water, providing target chromium concentrations equivalent to 10 mg/L in solution. Five-mL aliquots of the 10-fold dilutions were transferred to 100-mL volumetric flasks for the DPC spectrophotometric analyses, providing target chromium concentrations equivalent to 0.5 mg/L in solution. After addition of 2 mL of the DPC reagent solution, the addition of 2 mL of 10 percent (v/v) sulfuric acid was required to adjust the pH of the test sample solutions within the specified pH range.

Total chromium concentrations were measured in 10-fold dilutions of the original sample filtrates by ICP-OES. All calibration and control check standards were prepared in an aqueous 0.1 percent (w/v) potassium persulfate matrix solution to approximate the final matrix of the test sample solutions.

The results for the chromium analyses of the test samples using aqueous persulfate digestions are summarized in TABLE 31. Approximately 73 percent of the endogenous Cr(VI) was recovered from the duplicate barium chromate test samples digested in the persulfate medium as determined by DPC spectrophotometry; approximately 78 percent of endogenous Cr(VI) was recovered

TABLE 31. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF HEXAVALENT AND TRIVALENT CHROMIUM COMPOUNDS USING PERSULFATE DIGESTIONS

Test Experiment	DPC		ICP	
	(1)	(2)	(1)	(2)
Recovery of Cr(VI), Percent(a)	74	72	79	78
Oxidation of Cr(III), Percent(b)	90	83	--	--
Recovery of Cr(III), Percent(b)	--	--	94	87

(a) Based on analyses of $BaCrO_4$ masses equivalent to 100 mg Cr(VI).

(b) Based on analyses of $Cr(NO_3)_3 \cdot 9H_2O$ masses equivalent to 100 mg Cr(III).

by ICP-OES. Approximately 86 percent of the endogenous Cr(III) in the duplicate chromium nitrate test samples was oxidized to Cr(VI) in the persulfate medium as determined by DPC spectrophotometry; approximately 90 percent of the endogenous Cr(III) was recovered from the duplicate chromium nitrate test samples in the persulfate medium as determined by ICP-OES.

Separate aliquots of digest solutions from each of the barium chormate and chromium nitrate test samples were spiked with 30 mg of aqueous Cr(VI) as potassium dichromate at the instrument (post-digestion spikes) to ascertain whether the observed redox phenomena resulted in the persulfate digestions or from multiplicative interferences in the DPC quantification measurements. Hexavalent chromium spike recoveries of 84 percent and 92 percent were measured for the barium chromate digest solution and the chromium nitrate digest solution, respectively. Although the 92 percent spike recovery is satisfactory, the 84 percent recovery of Cr(VI) in the barium chromate digest solution is relatively low. The low recovery may be due to the formation of barium chromate resulting from a reaction between the Cr(VI) spike with barium ions in solution although this was not experimentally verified.

Endogenous Cr(VI) in test portions of barium chromate, equivalent to 100 mg Cr(VI), was recovered to the extents of approximately 73 percent by DPC spectrophotometry and approximately 78 percent by ICP-OES. The mechanism for the solubilization of the barium chromate test compounds in the persulfate digestion medium is inconclusive. A possible mechanism involves dissolution of Cr(VI) from barium chromate by preferential precipitation of barium sulfate where sulfate is produced via redox by the reduction of persulfate. Due to the similarities in solubilities of barium chromate ($K_{sp} = 2.4 \times 10^{-10}$) and barium sulfate ($K_{sp} = 1.3 \times 10^{-10}$), it is inconclusive whether or not the sulfate concentration in solution would be high enough to preferentially precipitate barium sulfate.

Oxidation of Cr(III) in the chromium nitrate test samples to the extent of approximately 86 percent may possibly be explained by a redox reaction between Cr(III) and persulfate based on the following half-reactions:

$$S_2O_8^{-2} + 2e^- \longleftrightarrow 2SO_4^{-2} \qquad E^o = +\ 2.01\ V$$

$$Cr^{+3} + 4H_2O \longleftrightarrow HCrO_4^- + 7H^+ + 3e^- \qquad E^o = -\ 1.195\ V$$

Even though insoluble chromates, such as barium chromate, may be solubilized to a large extent, the persulfate medium is not recommended for digestions of solid environmental samples because of the relative ease in oxidation by persulfate of Cr(III) that may be endogenous in the original samples.

PHASE IV - ANALYSES OF ENVIRONMENTAL SAMPLES

The Cr(VI) spike experiments were not designed to investigate the solubilization properties of the alkaline digestion medium; the Cr(VI) spikes were added as soluble potassium dichromate solutions in order to test only the redox properties of the alkaline digestion medium.

River Sediment - Alkaline Digestions

The texture of SRM 1645 made it difficult to wet completely upon addition of the alkaline digestion medium; sample particles had a tendency to creep up the beaker wall during the digestion. When the digests were vacuum filtered, a brown precipitate from each SRM test portion was retained on the filter medium. The colors of all digest solutions were yellow of varying intensities; the digest solutions from the SRM test portions spiked with Cr(VI) exhibited the brightest yellow colors. The pH of each of the 1-L digest solutions was approximately 11.

The results for the chromium analyses of test portions of NBS-SRM 1645 using alkaline digestions are summarized in TABLE 32. Approximately 0.7 mg/g of chromium was measured in the unspiked samples by both DPC spectrophotometry and ICP-OES. The chromium concentrations measured by ICP-OES represent approximately 3 percent of the certified chromium concentration. The low recovery by ICP-OES indicates that only 3 percent of the endogenous chromium in the river sediment was solubilized in the alkaline medium. The same concentration of chromium measured in the digest solutions by the two techniques suggests that all of the solubilized chromium was hexavalent chromium. However, it is not known whether the chromium measured by DPC spectrophotometry was due to endogenous Cr(VI) in the sample or that part of the solubilized chromium was initially Cr(III) which was oxidized to Cr(VI) during the digestion.

TABLE 32. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF NBS-SRM 1645 (RIVER SEDIMENT) USING ALKALINE DIGESTIONS

Test Experiment	DPC		ICP	
	(1)	(2)	(1)	(2)
Cr(VI) Measured, mg/g	0.74	0.74	--	--
Total Cr Measured, mg/g	--	--	0.75	0.77
Recovery of Certified Cr[(a)], Percent	--	--	3	33
Recovery of Cr(VI) Spike[(b)], Percent	96	95	99	100
Oxidation of Cr(III) Spike[(c)], Percent	2	4	--	--
Recovery of Cr(III) Spike[(c)], Percent	--	--	3	5

(a) Certified chromium concentration is 29.6 mg/g (uncertainty is 2.8 mg/g).

(b) One gram of SRM 1645 spiked with 30 mg Cr(VI).

(c) One gram of SRM 1645 spiked with 30 mg Cr(III).

Recoveries of Cr(VI) spikes were 96 percent by DPC spectrophotometry and 100 percent by ICP-OES. The complete recoveries indicate that the Cr(VI) spikes are not reduced in the river sediment in the alkaline digestion medium.

Analyses of Cr(III) spike solutions by DPC spectrophotometry revealed that approximately 2-fold higher concentrations of Cr(VI) were measured relative to the unspiked samples. The increase in measured Cr(VI) concentrations indicated that the Cr(III) spikes were oxidized to some extent to Cr(VI) in the alkaline digestion medium; 3 percent oxidation of Cr(III) was observed. For the present test conditions with an approximate 40-fold ratio of Cr(III) to Cr(VI), 3 percent oxidation of the Cr(III) spikes resulted in a 100 percent measurement error for Cr(VI). The ICP-OES analyses revealed approximately a 4 percent recovery of the Cr(III) spikes. The low recoveries of Cr(III) spikes by ICP-OES were due to precipitation of Cr(III) in the alkaline digestion medium.

River Sediment - Nitric Acid Digestions

The SRM samples wetted more effectively in the 50 percent nitric acid digestion medium than in the alkaline digestion medium. When the digest solutions were filtered, a brown precipitate from each SRM test sample was retained on the filter medium. The colors of the sample filtrates were varying shades of green.

The ICP-OES analyses for total chromium measurements were performed on the 1-L digest solutions. The DPC spectrophotometric measurements were performed on 10-fold dilutions of the 1-L filtrate solutions for each of the six SRM samples. The pH of each of the 10-fold dilutions was approximately 1.5 from the residual nitric acid present.

The diluted samples were colorless and clear in appearance before addition of DPC. However, upon addition of the DPC reagent to each of the SRM test samples, the sample solutions turned a golden or yellow-brown color instead of the red-violet color expected. Since the yellow color changes were not observed when DPC was added to the reagent blank and chromium calibration standards, the yellow-brown color resulted from an interaction between the DPC and an unidentified sample matrix component. If an additive background interference is present, there is no easy method to compensate for it. A separate aliquot of the unspiked SRM solution, without the addition of DPC, was used as the reference solution for the DPC colorimetric analyses; the absorbance produced by this solution was approximately the same absorbances produced by the reagent blanks.

The results for the chromium analyses of test portions of NBS-SRM 1645 using nitric acid digestions are summarized in TABLE 33. Approximately 0.1 mg/g of chromium was measured in the unspiked samples by DPC spectrophotometry. Approximately 27 mg/g of total chromium was measured by ICP-OES; the experimentally measured chromium concentration represents 93 percent of the certified chromium concentration. This compares favorably with the total chromium determinations by ICP-OES of 2.7 percent (27 mg/g) using the independent nitric acid-perchloric acid digestion method. The measured concentrations of total chromium by ICP-OES using both acid digestion methods are within the uncertainty limits of the certified chromium concentration, 2.96 percent, in NBS-SRM 1645 River Sediment. The complete recovery of chromium, within the uncertainty limits of the certified chromium concentration, by ICP-OES indicates that the entire amount of endogenous chromium in the SRM was solubilized in the nitric acid digestion medium. However, based only on the results from analyses of the unspiked SRM samples, it is not known whether the solubilized chromium was due completely to endogenous Cr(III) or whether Cr(VI), originally present in the sample, was later reduced to Cr(III) in the nitric acid digestion medium.

Recoveries of Cr(VI) spikes by ICP-OES were approximately 106 percent; no amount of the Cr(VI) spikes was recovered by DPC spectrophotometry. The results indicate that the soluble Cr(VI) spikes in the SRM river sediment were completely reduced to Cr(III) in the nitric acid digestion medium.

Analyses of the SRM samples spiked with Cr(III) by DPC spectrophotometry revealed no increase in measured chromium concentrations relative to the unspiked samples. The DPC spectrophotometic results indicate that the Cr(III) spikes in the SRM river sediment were not oxidized to Cr(VI) in the nitric acid digestion medium. Approximately 104 percent reeovery of the Cr(III) spikes by ICP-OES was determined indicating that Cr(III) was soluble in the nitric acid digestion medium.

The potential existence of a positive additive interference in the DPC spectrophotometric measurements was not rigorously examined. Approximately 0.1 mg/g of chromium was measured for each of the spiked and unspiked SRM samples. Since it was determined that the SRM river sediment digested in a

TABLE 33. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF NBS-SRM 1645 (RIVER SEDIMENT) USING ACID DIGESTIONS

Test Experiment	DPC (1)	DPC (2)	ICP (1)	ICP (2)
Cr(VI) Measured, mg/g	0.1	0.1	--	--
Total Cr Measured, mg/g	--	--	27.4	27.5
Recovery of Certified Cr[a], Percent	--	--	93	93
Recovery of Cr(VI) Spike[b], Percent	0	0	107	106
Oxidation of Cr(VI) Spike[c], Percent	0	0	--	--
Recovery of Cr(III) Spike[c], Percent	--	--	101	108

(a) Certified chromium concentration is 29.6 mg/g (uncertainty is 2.8 mg/g).

(b) One gram of SRM 1645 spiked with 30 mg Cr(VI).

(c) One gram of SRM 1645 spiked with 30 mg Cr(III).

nitric acid medium is a reducing matrix, it is probable that the small measured absorbances were due to the constant background interference produced by the yellow-brown color rather than due to Cr(VI) present in the sample solutions. However, even with the presence of this type of additive, background interference in the present DPC spectrophotometric analyses, the conclusions regarding the solubility and redox behavior of chromium species in the nitric acid digestion medium described above remain valid.

Municipal Digested Sludge - Alkaline Digestions

The sample filtrate solutions were yellow-brown in color and clear in appearance. The pH of each filtrate solution was approximately 12. Concentrated nitric acid was added to adjust the pH of the filtrate solutions to slightly less than 7 prior to DPC spectrophotometric analyses. After addition of the DPC reagent to the sample solutions, the pH of the filtrate solutions was adjusted to 2 with the addition of concentrated sulfuric acid. Upon adjustment of the pH of the sample solutions to approximately 2 with sulfuric acid, the solutions turned cloudy; this appearance was observed even if DPC was not present in the sample solution. These sample solutions were again vacuum-filtered in an attempt to remove the newly formed particulate matter.

The precipitates that were retained on the filter membranes were brown; the filtrate solutions retained only a light-yellow tint. These filtrate solutions were analyzed for Cr(VI) within 10 to 15 minutes after DPC addition, acidification with sulfuric acid and secondary filtration. Test sample filtrates, taken through the same pH adjustment and secondary filtration steps but without the addition of DPC, were used as reference solutions in the DPC spectrophotometric analyses.

The results for the chromium analyses of test portions of Municipal Digested Sludge (MDS) using alkaline digestions are summarized in TABLE 34. No detectable chromium was measured in the unspiked samples by either DPC spectrophotometry (less than 0.01 mg/g of chromium) or ICP-OES (less than 0.05 mg/g of chromium). The ICP-OES data indicate that, based on a detection limit of approximately 0.05 mg/g, less than 25 percent of the endogenous chromium in the MDS sample was solubilized in the alkaline digestion medium. The additional dilution required because of the filtration difficulties decreased

TABLE 34. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF MUNICIPAL DIGESTED SLUDGE USING ALKALINE DIGESTIONS

Test Experiment	DPC (1)	DPC (2)	ICP (1)	ICP (2)
Cr(VI) Measured, mg/g	<0.01	<0.01	--	--
Total Cr Measured, mg/g	--	--	<0.05	<0.05
Recovery of Reference Cr[(a)], Percent	--	--	<25	<25
Recovery of Cr(VI) Spike[(b)], Percent	<5	<5	<25	<25
Oxidation of Cr(III) Spike[(c)], Percent	<5	<5	--	--
Recovery of Cr(III) Spike[(c)], Percent	--	--	<25	<25

(a) Reference chromium concentration is 0.204 mg/g (uncertainty is 0.090 mg/g).

(b) One gram of Municipal Digested Sludge spiked with 0.2 mg Cr(VI).

(c) One gram of Municipal Digested Sludge spiked with 0.2 mg Cr(III).

the chromium concentration in solution so that it could not be reliably measured by ICP-OES. The DPC spectrophotometric data indicate that, based on a detection limit of approximately 0.01 mg/g, less than 5 percent of the endogenous chromium was hexavalent chromium.

No detectable chromium was measured in the MDS samples spiked with Cr(VI) by either DPC spectrophotometry or ICP-OES. Based on the same respective detection limits for the two measurement techniques, less than 5 percent of the Cr(VI) spike was recovered by DPC spectrophotometry and less than 25 percent of the Cr(VI) spike was recovered by ICP-OES. These data indicate that the Cr(VI) spikes are reduced in Municipal Digest Sludge even in the alkaline digestion medium and the Cr(III) is then precipitated under such highly alkaline conditions.

Chromium was also not detected in the MDS samples spiked with Cr(III) by either DPC spectrophotometry or ICP-OES. Based on the same respective detection limits for the two measurement techniques, less than 5 percent oxidation of the Cr(III) spikes was determined by DPC spectrophotometry; less than 25 percent recovery of the Cr(III) spikes was determined by ICP-OES. These data indicate that the Cr(VI) spikes are only slightly oxidized, if at all, in Municipal Digest Sludge in the alkaline digestion medium. The low recoveries of the Cr(III) spikes by ICP-OES confirm that Cr(III) is precipitated in the alkaline digestion medium.

Municipal Digested Sludge - Nitric Acid Digestions

The gelatinous precipitates that formed with the MDS samples in the alkaline digestion medium were not present in the nitric acid digestion medium. The solid material remaining in the sample digests was not gelatinous but rather exhibited a silt- or sediment-like appearance. Filtration of the acid digests proceeded rapidly. The filtrates were clear in appearance and exhibited bright yellow-orange colors; the precipitates retained on the filter media appeared to have the texture of sediment and were grey in color. The pH of each of the 100-mL filtrates was less than 1.

An unspiked MDS sample filtrate, without the addition of DPC, was used as the reference solution in the DPC spectrophotometric analyses. Upon addition of the DPC reagent to each of the MDS test samples, the sample solutions turned a darker shade of yellow-brown color. Similar to the observations of nitric acid digestions of NBS-SRM 1645 River Sediment, the yellow-brown color resulted from interaction between the DPC and an unidentified sample matrix component.

The results for the chromium analyses of test portions of Municipal Digested Sludge using nitric acid digestions are summarized in TABLE 35. Approximately 0.03 mg/g of hexavalent chromium was measured in the unspiked samples by DPC spectrophotometry. Approximately 0.18 mg/g of total chromium was measured in the unspiked MDS samples by ICP-OES; the chromium concentrations measured by ICP-OES represent approximately 91 percent of the reference chromium concentration. This concentration value compares favorably with the total chromium concentration of 194 ug/g measured by ICP-OES using an independent nitric acid-perchloric acid digestion. Both total chromium concentration values are within the 95 percent confidence limits of the 204 ug/g reference concentration value as determined from analyses by EPA reference laboratories.

The complete recovery of total endogenous chromium, within the concentration uncertainty limits, as determined by ICP-OES indicates that the total amount of endogenous chromium in the MDS matrix was solubilized in the nitric acid digestion medium and that Cr(III) does not precipitate under such acidic conditions. The much lower chromium concentrations measured by DPC spectrophotometry indicate that the endogenous chromium in the MDS samples was either Cr(III) or that any endogenous Cr(VI) was reduced to Cr(III) in the nitric acid digestion medium.

Recoveries of Cr(VI) spikes were approximately 2 percent by DPC spectrophotometry and 95 percent by ICP-OES. The low recoveries by DPC spectrophotometry indicate that Cr(VI) spikes in the MDS samples are reduced in the nitric acid digestion medium. The complete recoveries of Cr(VI) spikes by ICP-OES indicate that, although reduction apparently occurs, the Cr(III) remains soluble in the nitric acid digestion medium.

Analyses of Cr(III) spike solutions by DPC spectrophotometry revealed that no significant oxidation occurred. The 95 percent recoveries of Cr(III) spikes to the MDS samples by ICP-OES confirm that Cr(III) is highly soluble in the nitric acid digestion medium.

The potential existence of the positive additive interference in the DPC spectrophotometric measurements was not rigorously examined. Approximately 0.03 to 0.04 mg/g of chromium was measured by DPC spectrophotometry in all of

TABLE 35. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF MUNICIPAL DIGESTED SLUDGE USING ACID DIGESTIONS

Test Experiment	DPC		ICP	
	(1)	(2)	(1)	(2)
Cr(VI) Measured, mg/g	0.034	0.032	--	--
Total Cr Measured, mg/g	--	--	0.189	0.182
Recovery of Reference Cr[a], Percent	--	--	93	89
Recovery of Cr(VI) Spike[b], Percent	3	2	96	94
Oxidation of Cr(III) Spike[c], Percent	0	1	--	--
Recovery of Cr(III) Spike[c], Percent	--	--	96	94

(a) Reference chromium concentration is 0.204 mg/g (uncertainty is 0.090 mg/g).

(b) One gram of Municipal Digested Sludge spiked with 0.2 mg Cr(VI).

(c) One gram of Municipal Digested Sludge spiked with 0.2 mg Cr(III).

the unspiked and spiked MDS digest solutions. This suggests that the measured abosrbances may not be due to Cr(VI) but rather due to a constant additive background interference from the yellow-brown color formed when DPC was added to the MDS digest solutions. However, even if such an additive background interference is present, the general conclusions described above regarding the redox and solubilization behavior of chromium species in the nitric acid digestion medium remain valid.

Contaminated Soil "A" - Alkaline Digestions

When the digest samples were vacuum-filtered, a grey-brown precipitate was retained on the filter membrane for each of the soil samples. The colors of the filtrate solutions were varying shades of brown. Upon addition of DPC and acifification to pH 2 with sulfuric acid, the sample solutions turned various shades of red-violet indicating proper color development for Cr(VI) when an obvious color interference is not present.

The results for the chromium analyses of test portions of Contaminated Soil "A" using alkaline digestions are summarized in TABLE 36. Approximately 0.1 mg/g of chromium was measured in the unspiked samples by both DPC spectrophotometry and ICP-OES. The chromium concentrations measured by ICP-OES represent approximately 11 percent of th pre-analyzed chromium concentration. The low recoveries by ICP-OES indicate that approximately 11 percent of the endogenous chromium in Soil "A" was solubilized in the alkaline digestion medium. The same concentrations of chromium measured in the digest solutions by both techniques suggest that all of the solubilized chromium was hexavalent chromium. However, it is not conclusively known whether the chromium measured by DPC spectrophotometry was due to endogenous Cr(VI) in the sample or whether part of the solubilized chromium was initially Cr(III) which was oxidized to Cr(VI) during the alkaline digestion.

Recoveries of Cr(VI) spikes were 92 percent by DPC spectrophotometry and 96 percent by ICP-OES. The complete recoveries by both techniques indicate that the Cr(VI) spikes were not reduced in the soil sample in the alkaline digestion medium.

Analyses of Cr(III) spike solutions by DPC spectrophotometry revealed that approximately 2-fold higher concentrations of Cr(VI) were measured relative to the unspiked samples. The increase in measured Cr(VI)

TABLE 36. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF CONTAMINATED SOIL SAMPLE "A" USING ALKALINE DIGESTIONS

Test Experiment	DPC (1)	DPC (2)	ICP (1)	ICP (2)
Cr(VI) Measured, mg/g	0.10	0.12	--	--
Total Cr Measured, mg/g	--	--	0.105	0.125
Recovery of Pre-Analzyed Cr(a), Percent	--	--	10	12
Recovery of Cr(VI) Spike(b), Percent	94	91	96	95
Oxidation of Cr(III) Spike(c), Percent	10	13	--	-
Recovery of Cr(III) Spike(c), Percent	--	--	10	15

(a) Pre-analyzed chromium concentration is approximately 1 mg/g.

(b) One gram of Soil "A" spiked with 1 mg Cr(VI).

(c) One gram of Soil "A" spiked with 1 mg Cr(III).

concentrations indicated that the Cr(III) spikes were oxidized to some extent in the alkaline digestion medium; approximately 12 percent oxidation was observed. For the present test conditions with an approximate 10-fold ratio of Cr(III) to Cr(VI), the 12 percent oxidation of the Cr(III) spikes resulted in a 100 percent measurement error for Cr(VI). The ICP-OES analyses revealed approximately a 12 percent recovery of the Cr(III) spikes. The low recoveries of Cr(III) spikes by ICP-OES were due to precipitation of Cr(III) in the alkaline digestion medium.

Contaminated Soil "A" - Nitric Acid Digestions

A precipitate was retained on the filter medium; the filtrate was yellow-brown in color. Upon addition of DPC to the diluted filtrates, the clear, colorless solutions turned yellow-brown, not the red-violet color expected for Cr(VI). This color formation may represent a similar additive background interference observed in the previous acid digestion experiments.

The results for the chromium analyses of test portions of Contaminated Soil "A" using nitric acid digestions are summarized in TABLE 37. No measurable hexavalent chromium was detected by DPC spectrophotometry; this corresponds to less than 0.05 mg/g of Cr(VI) in the soil sample. An average chromium concentration of 1.04 mg/g was measured by ICP-OES in the unspiked soil samples, representing 104 percent of the pre-analyzed chromium concentration. This concentration value compares favorably with 0.10 mg/g of total chromium measured by ICP-OES following the independent nitric acid-perchloric acid digestion method. Both concentration values for total chromium are also in good agreement with the pre-analyzed concentration value of approximately 0.1 mg/g as determined by independent analysts.

The results of the ICP-OES analyses indicate that all of the endogenous chromium in Contaminated Soil "A" was solubilized in the acid medium. However, it is not known from these data whether the endogenous chromium was Cr(III) or whether the endogenous chromium was Cr(VI) which was reduced to Cr(III) in the nitric acid digestion.

No detectable hexavalent chromium was measured in Contaminated Soil "A" spiked with Cr(VI) by DPC spectrophotometry; this corresponds to less than 5 percent recovery of the Cr(VI) spikes based on our detection limit for DPC spectrophotometry. The average recovery of the Cr(VI) spikes by ICP-OES was

TABLE 37. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF CONTAMINATED SOIL "A" USING ACID DIGESTIONS

Test Experiment	DPC		ICP	
	(1)	(2)	(1)	(2)
Cr(VI) Measured, mg/g	<0.05	<0.05	--	--
Total Cr Measured, mg/g	--	--	1.03	1.06
Recovery of Pre-Analyzed Cr[a], Percent	--	--	103	106
Recovery of Cr(VI) Spike[b], Percent	<5	<5	99	97
Oxidation of Cr(III) Spike[c], Percent	<5	<5	--	--
Recovery of Cr(III) Spike[c], Percent	--	--	93	96

(a) Pre-analyzed chromium concentration is approximately 1 mg/g.

(b) One gram of Soil "A" spiked with 1 mg Cr(VI).

(c) One gram of Soil "A" spiked with 1 mg Cr(III).

approximately 98 percent. These spike recovery data indicate that the Cr(VI) spikes are reduced to Cr(III) in the nitric acid digestion medium and that Cr(III) is soluble under such highly acidic conditions.

Recoveries of post-digestion Cr(VI) spikes were approximately 94 percent. These data indicate that reduction of the Cr(VI) spikes in Contaminated Soil "A" occur in the nitric acid digestion and not in the DPC colorimetric measurement.

No measurable hexavalent chromium was detected in Contaminate Soil "A" spiked with Cr(III) by DPC spectrophotometry; this corresponds to less than 5 percent oxidation of the Cr(III) spikes based on our detection limit. The average recovery of the Cr(III) spikes by ICP-OES was approximately 94 percent. These spike recovery data indicate that the Cr(III) spikes are not significantly oxidized to Cr(VI) in the nitric acid digestion medium and that the Cr(III) spikes do not precipitate under these acidic conditions.

Contaminated Soil "B" - Alkaline Digestions

The results for the chromium analyses of test portions of Contaminated Soil "B" following alkaline digestions are presented in TABLE 38. Approximately 0.2 mg/g of hexavalent chromium was measured in the unspiked sample solutions by both DPC spectrophotometry and ICP-OES. The chromium concentrations measured in the alkaline digest solutions by ICP-OES represent approximately 2 percent of the pre-analyzed chromium concentration (9.3 mg/g) following the nitric acid-perchloric acid digestion. The low recoveries of endogenous chromium by ICP-OES indicate that approximately 2 percent of the endogenous chromium in this contaminated soil sample was solubilized in the alkaline digestion medium. It is not known conclusively whether the chromium measured by DPC spectrophotometry was due to endogenous hexavalent chromium in the soil sample or whether part of the solubilzed chromium was initially Cr(III) which was oxidized to Cr(VI) during the alkaline digestion.

Recoveries of Cr(VI) spikes were approximately 95 percent by DPC spectrophotometry and approximately 94 percent by ICP-OES. The complete recoveries indicate that the Cr(VI) spikes were not reduced in the contaminated soil in the alkaline digestion medium.

Post-digestion spike recoveries of 101 percent and 100 percent were obtained by DPC spectrophotometry indicating the absence of a multiplicative

TABLE 38. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF CONTAMINATED SOIL "B" USING ALKALINE DIGESTIONS

Test Experiment	DPC (1)	DPC (2)	ICP (1)	ICP (2)
Cr(VI) measured, mg/g	0.18	0.21	--	--
Total Cr measured[a], mg/g	--	--	0.24	0.22
Recovery of Pre-analyzed Cr[a], Percent	--	--	3	2
Recovery of Cr(VI) Spike[b], Percent	93	97	93	94
Oxidation of Cr(III) Spike[c], Percent	2	3	--	--
Recovery of Cr(III) Spike[c], Percent	--	--	3	2

(a) Pre-analyzed chromium concentration is 9.3 mg/g (wet weight).

(b) One gram of Soil "B" spiked with 8.5 mg Cr(VI).

(c) One gram of Soil "B" spiked with 8.5 mg Cr(III).

interference in the quantification step. A post-digestion spike recovery of 100 percent by ICP-OES was obtained indicating the absence of a multiplicative interference in the ICP-OES quantification step.

Analyses of Cr(III)-spiked solutions by DPC spectrophotometry revealed that approximately 2-fold higher concentrations of Cr(VI) were measured relative to the unspiked samples solutions. The increase in measured Cr(VI) concentrations indicated that the Cr(III) spikes were oxidized to some extent to Cr(VI) in the alkaline digestion medium; approximately 2 percent oxidation of Cr(III) was observed. For the present test conditions with an approximate 40-fold ratio of Cr(III) to Cr(VI), 2 percent oxidation of the Cr(III) spikes resulted in 100 percent errors for Cr(VI) measurements. The ICP-OES analyses revealed approximately 2 percent recovery of the Cr(III) spikes. The low recoveries of Cr(III) spikes by ICP-OES were due to precipitation of Cr(III) in the alkaline digestion medium.

Investigation of the Extents of Oxidation of Cr(III) Spikes in Contaminated Soil "B" for Different Cr(III) to Endogenous Cr(VI) Concentration Ratios

To determine whether larger spikes would result in a proportional increase in Cr(III) oxidation, eight 1-g samples were used to form 4 different sample sets: (1) duplicate unspike samples, (2) duplicate samples spiked with 9.3 mg of Cr(III), (3) duplicate samples spiked with 18.6 mg Cr(III), and (4) duplicate samples spiked with 46.5 mg Cr(III). Spikes were added as appropriate aliquots of a 9.3 mg/mL Cr(III) standard prepared in deionized water.

Digestion, vacuum-filtration and neutralization of all samples proceeded as described previously. Gelatinous precipitates formed upon neutralization of the filtrate solutions. The precipitates were extremely fine which severely clogged the filter membranes. After the solids had settled, one mL was withdrawn from each filtrate solution and diluted to 100 mL for DPC spectrophotometric analysis.

The results for this study are summarized in TABLE 39. Oxidation of Cr(III) spikes remained at the 2 percent level for 9.3 mg/g and 18.6 mg/g Cr(III) spikes. The percent oxidation decreased to 1 percent for 46.5 mg/g Cr(III) spikes. Similar results were obtained by both DPC spectrophotometry

TABLE 39. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF CONTAMINATED SOIL "B" SPIKED AT DIFFERENT CONCENTRATIONS USING ALKALINE DIGESTIONS

Test Experiment	DPC		ICP	
	(1)	(2)	(1)	(2)
Cr(VI) measured, mg/g	0.20	0.19	--	--
Total Cr measured[(a)], mg/g	--	--	0.24	0.21
Recovery of Pre-analyzed Cr[(a)], Percent	--	--	3	2
Oxidation of 9.3 mg Cr(III) Spike, Percent	2.2	2.2	--	--
Recovery of 9.3 mg Cr(III) Spike, Percent	--	--	3.0	3.0
Oxidation of 18.6 mg Cr(III) Spike, Percent	1.7	1.6	--	--
Recovery of 18.6 mg Cr(III) Spike, Percent	--	--	1.4	1.7
Oxidation of 46.5 mg Cr(III) Spike, Percent	0.8	0.7	--	--
Recovery of 46.5 mg Cr(III) Spike, Percent	--	--	0.8	1.0

(a) Pre-analyzed chromium concentration is 9.3 mg/g (dry weight).

and ICP-OES analyses. This contaminated soil sample apparently contains sufficient oxidants to oxidize at least three times the endogenous chromium concentration. Such data indicate that the probable origin of measured hexavalent chromium is actually endogenous Cr(III) which is oxidized during the digestion.

Investigation of Heating Time on the Extent of Solubilization of Endogenous Cr(VI) from Contaminated Soil Sample "B" and on the Extent of Oxidation of Cr(III) Spikes

Four Contaminated Soil "B" samples were divided into two sample sets: (1) duplicate unspiked samples and (2) duplicate samples spiked with 9.3 mg Cr(III). Spikes were added as 1-mL aliquots of a 9.3 mg/mL Cr(III) standard prepared in deionized water.

Alkaline digestions of these samples were carried out at 80°C +/- 10°C, with mechanical stirring for 3 hours instead of the usual 45 minutes. This provides for a 4-fold increase in digestion time. The DPC spectrophotometric analyses of filtrates were performed on 100-fold dilutions of the filtrate. The ICP-OES analyses were performed on 2.5-fold dilutions of the filtrates.

The results from these analyses are summarized in TABLE 40. Solubilization of chromium was increased by extending the digestion time. After a 3-hour digestion period, 70 percent more hexavalent chromium was measured compared to the concentration obtained for the usual 45-minute digestions. Analyses by ICP-OES revealed a 125 percent increase in total chromium concentration for unspiked samples undergoing 3-hour digestions. For unspiked samples, about 75 percent of the increase in concentration occurs in the form of Cr(VI) as determined by DPC spectrophotometry. By difference, 50 percent of the increase in concentration is attributed to Cr(III).

Oxidation of Cr(III) spikes is 4 percent and this represents a 100 percent increase in the hexavalent chromium measurement of the unspiked samples. Recovery of Cr(III) spikes agrees well with the percent oxidation of Cr(III) spikes as determined by ICP-OES. Since the percent of chromium (III)

TABLE 40. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF CONTAMINATED SOIL "B" USING ALKALINE DIGESTIONS FOR EXTENDED DIGESTION PERIODS

Test Experiment	DPC (1)	DPC (2)	ICP (1)	ICP (2)
Cr(VI) Measured, mg/g	0.34	0.34	--	--
Total Cr Measured[(a)], mg/g	--	--	0.43	0.42
Recovery of Pre-analyzed Cr[(a)], Percent	--	--	5	5
Oxidation of Cr(III) Spike[(b)], Percent	4	4	--	--
Recovery of Cr(III) Spike[(b)], Percent	--	--	4	4

(a) Pre-analyzed chromium concentration is 9.3 mg/g (dry weight).

(b) One gram of Sample "B" spiked with 9.3 mg Cr(III).

oxidation had not increased dramatically and that the spikes still produced a 100 percent increase in hexavalent chromium measurement, solubilization, rather than oxidation, is the reaction promoted by the prolonged digestion.

Electroplating Sludge - Alkaline Digestions

The sample filtrates were clear and golden color. Brown solid material was retained on the filter membranes for all samples. The results for the chromium analyses of test portions of Electroplating Sludge using alkaline digestions are summarized in TABLE 41. Approximately 0.38 mg/g of hexavalent chromium was measured in the unspiked samples by both DPC spectrophotometry and ICP-OES. The total chromium concentrations measured by ICP-OES represent approximately 5 percent of the pre-analyzed chromium concentration of 7.7 mg/g as determined by ICP-OES following nitric acid-perchloric acid digestion. This measured concentration value is within 10 percent of the reference concentration value of 7 mg/g as determined by EPA laboratories.

The low recoveries of endogenous chromium by ICP-OES indicate that approximately 5 percent of the endogenous chromium in the electroplating sludge sample was solubilized in the alkaline digestion medium. The same concentrations of chromium measured in the sample digest solutions by both techniques suggest that all of the solubilized chromium was hexavalent chromium. Moreover, it is probable that the chromium measured by DPC colorimetry was due to endogenous Cr(VI) in the electroplating sludge sample.

Recoveries of Cr(VI) spikes were 91 percent by DPC spectrophotometry and 93 percent by ICP-OES. The complete recoveries by both techniques indicate that the Cr(VI) spikes were stable in the electroplating sludge sample in the alkaline digestion medium.

Post-digestion spike recoveries of 101 percent and 108 percent were obtained by DPC spectrophotometry and ICP-OES, respectively. Complete recoveries of Cr(VI) post-digestion spikes verified the absence of a multiplicative interference during the quantification steps of both methods.

Analyses of Cr(III)-spiked sample solutions by DPC spectrophotometry revealed no apparent increase in measured Cr(VI) concentrations relative to the unspiked electroplating sludge sample solutions. The DPC spectrophotometric results indicate that the Cr(III) spikes in the electroplating sludge sample were not oxidized to Cr(VI) in the alkaline digestion medium. The ICP-OES

TABLE 41. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF ELECTROPLATING SLUDGE USING ALKALINE DIGESTIONS

Test Experiment	DPC		ICP	
	(1)	(2)	(1)	(2)
Cr(VI) measured, mg/g	0.41	0.32	--	--
Total Cr measured[a], mg/g	--	--	0.43	0.35
Recovery of Pre-analyzed Cr[a], Percent	--	--	6	5
Recovery of Cr(VI) Spike[b], Percent	94	88	96	90
Oxidation of Cr(III) Spike[c], Percent	0	0	--	--
Recovery of Cr(III) Spike[c], Percent	--	--	0	0

(a) Pre-analyzed chromium concentration is 7.7 mg/g.

(b) One gram of Electroplating Sludge spiked with 8.5 mg Cr(VI).

(c) One gram of Electroplating Sludge spiked with 8.5 mg Cr(III).

analyses revealed no measurable recovery of the Cr(III) spikes confirming the precipitation of Cr(III) in the alkaline digestion medium and no oxidation of Cr(III) to soluble Cr(VI).

Combined Precision of Methods 3060 and 7196 for the Determination of Endogenous Cr(VI) in Electroplating Sludge

Nine 1-g unspiked portions of this sample were carried through the alkaline digestion procedure and the hexavalent chromium concentration determined by DPC spectrophotometry. After vacuum-filtration, a fine gelatinous precipitate formed within 5 minutes after adjusting the solution pH to 7 with nitric acid. Absorbance measurements were performed on filtered and unfiltered solutions; no significant differences were observed.

The results of the 9 determinations are presented in TABLE 42. An average Cr(VI) concentration value of approximately 0.33 mg/g was obtained with a relative precision of 15 percent. If one estimates the 95 percent confidence limit by using the probability parameter t, we obtain:

$$0.329 \text{ +/- } \frac{2.31\ (0.06)}{\sqrt{9}} = 0.329 \text{ mg/g +/- } 0.05 \text{ mg/g}$$

This means that 5 out of 100 times, an experimental value can be expected to deviate by +/- 0.05 mg/g or more. Such relatively high imprecision may be related to the presence of sparingly soluble chromates and variable degrees of solubilization in the alkaline digestion procedure.

Estuarine Sediment - Alkaline Digestions

Very dark brown solids resembling fine silt were retained on the filter membranes. Filtrate solutions were golden in color. Since the concentration of solubilized chromium was anticipated to be low in these sample digest solutions, minimum dilutions were used to conduct DPC spectrophotometric and ICP-OES analysis. To compensate for the brown color of the digest filtrates, a color blank for each sample was prepared using the same dilution ratios. No DPC color reagent was added for these blanks. The concentration of

TABLE 42. PRECISION OF HEXAVALENT CHROMIUM CONCENTRATIONS DETERMINED IN ELECTROPLATING SLUDGE USING ALKALINE DIGESTIONS AND DPC SPECTROPHOTOMETRY

Trial 1	0.363 mg/g
2	0.352 mg/g
3	0.244 mg/g
4	0.330 mg/g
5	0.385 mg/g
6	0.318 mg/g
7	0.427 mg/g
8	0.255 mg/g
9	0.290 mg/g

Average = 0.329 mg/g

Standard deviation = 0.06 mg/g

Relative Standard Deviation = 15 percent hexavalent chromium could be calculated by the net absorbance obtained by the absorbance differences between the samples and the color blanks.

The presence of multiplicative errors was checked by post-digestion Cr(VI) spiking of duplicate Cr(III)-spiked filtrates. Only 36 percent and 62 percent recoveries of 0.76 μg/mL Cr(VI) spikes were found by DPC spectrophotometry. An average recovery of 89 percent for the same spike concentration was found by ICP-OES.

For both pre-digestion and post-digestion spiked solutions, the color developed was a different shade of pink rather than the the usual red-violet color. This color may have been due to the golden brown background color of the filtrates or it may have been due to formation of a DPC complex with another metal in the sample.

The results for the chromium analyses of NBS-SRM 1646 Estuarine Sediment following alkaline digestions are presented in TABLE 43. Neither DPC spectrophotometry nor ICP-OES provided reliable measurements of solubilized chromium due to extremely low chromium concentrations. Chromium was not detected in the alkaline digest solutions by ICP-OES. The total chromium concentration measured by ICP-OES following the nitric acid-perchloric acid digestion procedure was 58 μg/g. This measured concentration value is approximately 76 percent of the certified value. The low concentration value for chromium may have been due to loss of chromium as chromyl chloride during the digestion or to suppression of the chromium emission signal from matrix effects in the ICP-OES measurement.

The DPC spectrophotometric measurements were plagued by matrix interferences. No oxidation of Cr(III) spikes was found by DPC spectrophotometry. Confirmation of this result by ICP analyses indicated that Cr(III) spikes precipitated during the alkaline digestions. Only 34 percent of the Cr(VI) spikes were recovered indicating that Estuarine Sediment represents a reducing matrix. This reducing matrix may be a result of the high organic content (about 50 percent) and a significant level of sulfur (1 percent). Although no conclusive statement can be made about the chemical states of endogenous chromium in Estuarine Sediment, it is plausible that most of the hexavalent chromium measured was the residual portion of partially soluble or completely soluble chromates within the sample.

TABLE 43. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF NBS-SRM 1646 (ESTUARINE SEDIMENT) USING ALKALINE DIGESTIONS

Test Experiment	DPC		ICP	
	(1)	(2)	(1)	(2)
Cr(VI) Measured, mg/g	0.0019	0.0013	--	--
Total Cr Measured[a], mg/g	--	--	<0.005	<0.005
Recovery of Certified Cr[a], Percent	--	--	<7	<7
Recovery of Cr(VI) Spike[b], Percent	34	34	88	76
Oxidation of Cr(III) Spike[c], Percent	0	0	--	--
Recovery of Cr(III) Spike[c], Percent	--	--	0	3

(a) Certified chromium concentration is 0.076 mg/g (uncertainty is 0.003 mg/g).

(b) One gram of NBS-SRM 1646 spiked with 0.076 mg Cr(VI).

(c) One gram of NBS-SRM 1646 spiked with 0.076 mg Cr(III).

Tannery Sludge "A" (Low-Sulfide) - Alkaline Digestions

Upon addition of the alkaline digestion medium, the following observations were noted for each of the three sample sets: (1) the duplicate unspiked sample solutions remained clear and colorless, (2) the duplicate sample solutions spiked with Cr(III) turned light-blue in color as expected, and (3) the duplicate sample solutions spiked with Cr(VI) turned light-green in color instead of the characteristic yellow color of dichromate solutions. After the digestions had proceeded for 10 minutes, all six sample solutions had turned a milky appearance; the duplicate unspiked sample solutions and one of the Cr(VI)-spiked sample solutions had a visible orange tint and the other three sample solutons had a visible grey-brown shade.

After the 45-minute alkaline digestions, the sample digest solutions were allowed to cool and then vacuum-filtered. All sample filtrate solutions were orange in color. Solid material remaining in the sample digest solutions was retained on the filter membranes for all samples. The solid material appeared to have the texture of very fine-grained silt.

The results for the chromium analyses of test portions of Tannery Sludge "A" (low-sulfide) using alkaline digestions are summarized in TABLE 44. Approximately 0.16 mg/g of hexavalent chromium was measured in the unspiked sample solutions by both DPC spectrophotometry and ICP-OES. The total chromium concentrations measured by ICP-OES following the alkaline digestions represent approximately 3 percent of the pre-analyzed chromium concentrations (approximately 5.8 mg/g) following nitric acid-perchloric acid digestions.

The concentrations of total chromium measured in triplicate subsamples by ICP-OES following nitric acid-perchloric acid digestions were 5.9 mg/g, 5.7 mg/g, and 5.8 mg/g on a wet-weight basis. The average measured chromium concentration of 5.8 mg/g is low relative to the pre-analyzed chromium concentration information (25 mg/g) submitted with this tannery sludge sample. However, if the chromium information value of 25 mg/g is based on a dry-weight, the 30-40 percent solids content will account for much of this discrepancy.

The low recoveries of endogenous chromium by ICP-OES following alkaline digestions indicate that approximately 3 percent of the endogenous chromium in this tannery sludge sample was solubilized in the alkaline digestion medium. The same concentrations of chromium measured in the digest solutions by both techniques suggest that all of the solubilized chromium was

TABLE 44. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF TANNERY SLUDGE "A" (LOW-SULFIDE) USING ALKALINE DIGESTIONS

Test Experiment	DPC (1)	DPC (2)	ICP (1)	ICP (2)
Cr(VI) Measured, mg/g	0.13	0.19	--	--
Total Cr Measured[a], mg/g	--	--	0.14	0.17
Recovery of Pre-analyzed Cr[a], Percent	--	--	2	3
Recovery of Cr(VI) Spike[b], Percent	95	95	95	96
Oxidation of Cr(III) Spike[c], Percent	1	1	--	--
Recovery of Cr(III) Spike[c], Percent	--	--	2	1

(a) Pre-analyzed chromium concentration is 5.7 mg/g (wet weight).

(b) One gram of Tannery Sludge "A" spiked with 5.7 mg Cr(VI).

(c) One gram of Tannery Sludge "A" spiked with 5.7 mg Cr(III).

hexavalent chromium. However, it is not known conclusively whether the chromium measured by DPC spectrophotometr was due to endogenous hexavalent chromium in the tannery sludge sample or whether part of the solubilized chromium was initially endogenous Cr(III) which was oxidized to Cr(VI) during the alkaline digestion.

Recoveries of Cr(VI) spikes were approximately 95 percent by both DPC spectrophotometry and ICP-OES. The complete recoveries by both techniques indicate that the Cr(VI) spikes were stable in this tannery sludge matrix in the alkaline digestion medium.

Post-digestion Cr(VI) spikes were added to the two unspiked sample digest solutions for each technique to check for a multiplicative interference during the quantification step. An average recovery of 102 percent was measured for 0.5 mg/L Cr(VI) spikes for DPC spectrophotometry; an average recovery of 102 percent was also measured for 1 mg/L Cr(VI) spikes for ICP-OES. The complete recoveries of post-digestion Cr(VI) spikes for both techniques confirmed the absence of a multiplicative interference in the quantification steps of the methods.

Analyses of Cr(III)-spiked solutions by DPC spectrophotometry revealed that approximately 1.5-fold higher concentrations of Cr(VI) were measured relative to the unspiked sample solutions. The increase in measured Cr(VI) concentrations indicated that the Cr(III) spikes were partially oxidized in the alkaline digestion medium; approximately 1 percent oxidation was observed. For the present test conditions with an approximate 35-fold ratio of Cr(III) to Cr(VI), the 1 percent oxidation of Cr(III) spikes resulted in a 50 percent error for Cr(VI) measurements. However, implications of oxidation of Cr(III) spikes in this tannery sludge sample should be viewed in light of the relatively high imprecision associated with the DPC spectrophotometric measurements in the low absorbance region (approximately twice the instrument detection limit) where the analyses were performed.

The ICP-OES analyses revealed approximately a 2 percent recovery of the Cr(III) spikes. The low recoveries of Cr(III) spikes by ICP-OES were due to precipitation of Cr(III) in the alkaline digestion medium.

Tannery Sludge "B" - Alkaline Digestions

Upon addition of the alkaline digestion medium, the duplicate sample solutions spiked with Cr(III) initially formed light-blue precipitates which redissolved as more alkaline digestion medium was added. This observation was later determined in a separate experiment to be a reaction between Cr(III) and the alkaline digestion medium. After digestion, all hairs in the samples had disappeared, but the solutions contained gelatinous grey-brown solids. These solutions were very slow to filter, and the resultant filtrates were golden brown in color. When neutralized, the filtrates became cloudy and emitted a strong odor resembling that of hydrogen sulfide gas. Particles inducing the cloudiness could not be removed by filtration through 0.45-um filters. To compensate for the light scattering effect of these fine particles, color blanks were done for each sample.

DPC spectrophotometry was performed on diluted sample filtrates. The color blanks were made by taking sample filtrates of the same dilution through the same pH adjustment (to pH 2) but without addition of DPC. Filtration of these blanks was necessary since the addition of 10 percent (v/v) sulfuric acid caused increasing turbidity.

The results for chromium analyses of Tannery Sludge "B" following alkaline digestions are summarized in TABLE 45. Less than 0.01 mg/g of hexavalent chromium was measured in the unspiked samples by DPC spectrophotometry. Analyses of the same unspiked solutions by ICP-OES revealed that about 0.1 mg/g of total chromium was present, which represents 1 percent solubilization of endogenous chromium as previously determined by ICP-OES following nitric acid-perchloric acid digestions.

The concentrations of total chromium measured in duplicate samples by ICP-OES following nitric acid-perchloric acid digestions were 8.0 mg/g and 7.7 mg/g on a wet-weight basis. The average measured chromium concentration of 7.8 mg/g is low compared to the pre-analyzed chromium concentration information value (39 mg/g) submitted with this tannery sludge sample. However, if the chromium information value of 39 mg/g is based on a dry-weight, approximately 15 percent solids content will account for much of this discrepancy.

Due to the presence of unfilterable solids in the final test solutions for DPC spectrophotometry causing high background absorbances, net absorbance values close to the detection limit (0.01 mg/L) were obtained which

TABLE 45. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF TANNERY SLUDGE "B" (HIGH SULFIDE) USING ALKALINE DIGESTIONS

Test Experiment	DPC		ICP	
	(1)	(2)	(1)	(2)
Cr(VI) Measured, mg/g	0.01	0.008	--	-
Total Cr Measured[a], mg/g	--	--	0.11	0.11
Recovery of Pre-Analyzed Cr[a], Percent	--	--	1	1
Recovery of Cr(VI) Spike[b], Percent	84	77	93	82
Oxidation of Cr(III) Spike[c], Percent	0	0	--	--
Recovery of Cr(III) Spike[c], Percent	--	--	0	0

(a) Pre-analyzed chromium concentration is 7.8 mg/g (wet weight).

(b) One gram of Tannery Sludge "B" spiked with 7.8 mg Cr(VI).

(c) One gram of Tannery Sludge "B" spiked with 7.8 mg Cr(III).

resulted in poor precision. Moreover, it is not certain whether or not the sample color blanks provided an accurate compensation for the light scattering effect caused by the gelatinous particles.

Recoveries of Cr(VI) spikes averaged 81 percent by DPC spectrophotometry and 88 percent by ICP-OES. Post-digestion Cr(VI) spiking measured by DPC spectrophotometry and ICP-OES gave 101 percent and 104 percent recoveries, respectively. Complete recovery of these post-digestion spikes indicated the absence of multiplicative interferences in the quantification step in either technique. A comparison of the percent Cr(VI) recoveries for pre- and post-digestion spikes indicates that reduction of Cr(VI) spikes was probably due to the high-sulfide reducing environment.

Analysis of Cr(III)-spiked solutions by DPC spectrophotometry and ICP-OES revealed that no oxidation of Cr(III) spikes occurred. Furthermore, it can be inferred from ICP-OES results that Cr(III) spikes were removed by precipitation in the alkaline digestion medium.

River Water - Alkaline Digestions

The sample filtrates were clear and colorless. White precipitates which had formed during the alkaline digestions were retained on the filter membrane. No special problems were encountered in the DPC spectrophotometric procedure. Care was exercised to ensure that no outgassing occurred in the quartz cells during absorbance measurements.

The results for chromium analyses of river water following alkaline digestions are summarized in TABLE 46. An average concentration of 0.025 ug/mL Cr(VI) was measured in the unspiked samples by DPC spectrophotometry. Chromium in filtrates of the alkaline digest solutions was not detected by ICP-OES. The concentration of chromium in the river water after nitric acid digestion could not be determined since it was below the detection limit (50 ug/L in solution or 0.2 ug/mL in the original water sample).

Recoveries of Cr(VI) spikes averaged 100 percent by DPC and 104 percent by ICP analyses. Approximately 1 percent oxidation of Cr(III) spikes was found by DPC spectrophotometry. This small percentage of oxidation is significant since 176 percent of the Cr(VI) was found in unspiked samples.

TABLE 46. SUMMARY OF RESULTS FOR CHROMIUM ANALYSES OF RIVER WATER USING ALKALINE DIGESTIONS

Test Experiment	DPC		ICP	
	(1)	(2)	(1)	(2)
Cr(VI) Measured, μg/g	0.027	0.023	--	-
Total Cr Measured[a], μg/g	--	--	<0.2	<0.2
Recovery of Pre-Analyzed Cr[a], Percent	--	--	--	--
Recovery of Cr(VI) Spike[b], Percent	99	100	104	103
Oxidation of Cr(III) Spike[c], Percent	1	1	--	-
Recovery of Cr(III) Spike[c], Percent	--	--	<10	<10

(a) Pre-analyzed chromium concentration is <0.2 μg/g (wet weight).

(b) Thirty grams of River Water spiked with 0.05 mg Cr(VI).

(c) Thirty grams of River Water spiked with 0.05 mg Cr(III).

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